

# Preparation and Characterization of Novel Polymer Hydrogel from Industrial Waste and Copolymerization of Poly(vinyl alcohol) and Polyacrylamide

Waleed K. El-Zawawy, Maha M. Ibrahim

Cellulose and Paper Department, National Research Center, El-Tahrir St., Dokki, Giza, Egypt

Received 4 June 2010; accepted 14 August 2011

DOI 10.1002/app.35481

Published online 30 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A novel hydrogel was prepared from industrial waste to form a green polymer with a higher swelling capacity. This hydrogel was synthesized by two methods for chemical crosslinking, namely crosslinking by radical polymerization and crosslinking by addition reaction. In crosslinking by radical polymerization, graft copolymerization of poly(vinyl alcohol) (PVA) and polyacrylamide (PAAm) was carried out using ceric ammonium sulfate in presence of *N,N'*-methylenebisacrylamide, and then mixed with the black liquor resulting from alkaline pulping of rice straw. While, in crosslinking by addition reaction, the same above reagents were mixed with the black liquor in absence of the initiator. The black liquor is an industrial waste resulting from the pulping method and consists of dissolved lignin and

carbohydrates. The black liquor causes environmental water pollution due to its dumping into the sea. The formed hydrogels were characterized using FT-IR spectroscopy and scanning electron microscopy (SEM). It was noted that the hydrogel prepared by radical polymerization showed high swelling capacity, 60.00%, compared to that prepared by the addition reaction, 27.27%. The hydrogels formed were used also to study the influence of sodium chloride on the absorption capacity at room temperature and swelling ratios at different temperatures and pHs. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4362–4370, 2012

**Key words:** hydrogel; graft copolymerization; black liquor; crosslinker

## INTRODUCTION

Hydrogels are polymeric networks, which absorb and retain large amounts of water. As the term “network” implies, crosslinks have to be present to avoid dissolution of the hydrophilic polymer chains/segments into the aqueous phase.<sup>1</sup> These crosslinked macromolecular structures are able to take up large quantities of water and biological fluids without dissolution. The biocompatibility of hydrogels is attributed to their ability to simulate tissues due to their high water content and their special surface properties. As a result of the resemblance between the synthetic and natural materials, these gels, which show a significant swelling change in response to external stimuli such as temperature,<sup>2–5</sup> pH,<sup>6,7</sup> ionic strength,<sup>8</sup> and electrical potential<sup>9,10</sup> have been investigated for applications ranging from solute separation<sup>11,12</sup> to controlled delivery of solutes.<sup>3–5,13</sup>

Water-soluble polymers owe their solubility properties to the presence of functional groups (mainly OH, COOH, NH<sub>2</sub>) which can be used for the formation of hydrogels. The polymerization of the vinyl derivatized water-soluble monomers can be carried out with an initiator forming hydrogels. Covalent bonds between systems composed of a peroxydisulfate and polymer chains can be established by the reaction with *N,N,N',N'*-tetramethylene-diamine (TEMED). This is a very efficient system, which gives rapid formation functional of the gel even under mild conditions (room temperature, pH 7).<sup>14,15</sup>

Chemically crosslinked gels can be obtained by different methods. One of the methods is radical polymerization, in which low molecular weight monomers are used in the presence of crosslinking agents. Another method is a crosslinking by addition reaction, in which water-soluble polymers can be converted into hydrogels using bis (or higher) functional crosslinking agents which react with functional groups of water-soluble polymers via addition reactions.<sup>1</sup>

Green polymeric material is a biodegradable material (neat polymer, blended product, or composite) obtained completely from renewable resources.<sup>16</sup> Because of their water-absorbing capacity, hydrogels are not only subject of investigation of researchers

Correspondence to: W. K. El-Zawawy (wkzawawy@yahoo.com).

Contract grant sponsor: Science and Technology Development Fund (STDF).

interested in fundamental aspects of swollen polymeric networks, but have also found widespread application in different technological areas, e.g., as materials for contact lenses and protein separation, matrices for cell-encapsulation and devices for the controlled release of drugs and proteins.

Agricultural residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic materials for paper, chemicals, and other technical products.<sup>17</sup> The major constituents of biofibers (lignocellulose) are cellulose, hemicellulose, and lignin.<sup>16</sup> Conventional technology for paper manufacture is based on digesting the raw material, (wood, recycled paper, and agricultural residues), which results in a black liquor. The black liquor is the liquor after it has been used in the digester is "spent" and contains high caustic, lignin, silica and high totally dissolved solids (TDS). Most of the paper industries which have black liquor concentration (in term of total dissolved solids) discard the liquor as it is or after some partial treatment to the river. Naturally, this leads to several water pollution problems. To be successful, the industry must find new ways to improve environmental and process performance.

The possibility of using the resulting black liquor in the synthesis of hydrogel is our aim in the present work. An investigation on the performance of the black liquor as a chemically crosslinked hydrogel with poly(vinyl alcohol) (PVA), polyacrylamide (PAAm) and *N,N'*-methylenebisacrylamide via both radical polymerization and addition reaction has been examined for the first time, to the best of our knowledge. *N,N'*-methylene-bisacrylamide acted as a low molecular weight monomer in case of the radical polymerization and as a bis functional crosslinker in case of the additional reaction. The synthesized soluble polymers, i.e., PVA and PAAm, were used for their functional groups that can bonded with the lignin present in the black liquor thus can form hydrogels. The nature of these hydrogels structures was characterized by scanning electron microscopy (SEM). Water absorption at different temperatures, as well as different pHs were discussed to show the difference between the two chemically crosslinked methods.

## EXPERIMENTAL

### Materials and methods

Black liquor resulting from alkaline pulping of rice straw with 10% sodium hydroxide was used as a lignin source. Poly(vinyl alcohol) (PVA), degree of polymerization (DP) of 1700–1800, and polyacrylamide (PAAm), molecular weight over 5,000,000, were provided from Qualikems and BDH, England, respectively. *N,N'*-methylene-bisacrylamide (NMBA) (SIGMA

Chemical), and ceric ammonium sulfate (CAS) (Wako-Pure Chemical), as an initiator, were used as received.

### Black liquor analysis

The black liquor resulting from alkaline pulping treatment of rice straw was analyzed for its main constituents using the Axios, Sequential WD\_XRF Spectrometer, PA Nalytical 2005.

The black liquor was neutralized first to pH 7.0 and the precipitated fraction was filtered in a Buchner funnel, and then washed with water. The final products were air-dried under ambient conditions and named as Fraction 1, and the resulting filtrate was then acidified to pH 4.0 and the precipitated fraction was filtered and washed till neutrality. The precipitate was then air-dried, named as Fraction 2 and stored for analysis.

After that, the pH of the new resulting filtrate was raised to pH 6.5 and the precipitate was collected and named as Fraction 3. Then the resulting filtrate was reacidified to pH 1.5 and the precipitate was collected and named as Fraction 4. Finally, the new filtrate was neutralized to pH 5.5 and the resulting precipitate, Fraction 5, was filtered and washed. The five fractions were tested for their solubility with dimethyl sulfoxide (DMSO) and the soluble fractions were analyzed by FT-IR and UV. The insoluble fractions, resulting from pH 7.0 and 6.5, i.e., Fractions 1 and 3, were characterized by EDX scanning electron microscope.

### Preparation of gel-film from the black liquor

Poly(vinyl alcohol) was first dissolved in water (10% w/v) at 60°C with a constant stirring. After cooling, a 0.12M of PAAm dissolved in 75 mL water was mixed with the PVA solution by stirring. To this solution, 0.1M CAS, as initiator, and the NMBA, as a crosslinker and monomer, was added, and the mixture was immediately stirred at 60°C for 3 h. The copolymerization reaction was continued up to 24 h with stirring at 25°C. After that, the black liquor in a ratio of 1 : 1 (lignin : PVA) was added to the copolymer solution and the reaction was stirred at 60°C. The formed gel was kept overnight at the same temperature then poured into a Petri-dish for film casting.

The same reaction was carried out without the presence of CAS to form a crosslinked gel by addition reaction.

### Measurement of equilibrium swelling ratio

The dried gels were immersed in an excess amount of distilled water at 25 and 50°C until swelling equilibrium was attained. Also, various pH solutions,

namely 2.7, 3.4, 4.4, 9.8, 10.7, and 11.5, and the dried gels were immersed in the different solutions at 25°C until swelling equilibrium was attained. Moreover, the dried gels were immersed in an excess amount of saline solutions (0.15M aqueous solutions of NaCl) at 25°C until swelling equilibrium was attained. The weight of wet sample ( $W_2$ ) was determined after removing the surface water by blotting with a filter paper. The weight of dry sample ( $W_1$ ) was determined after drying the gel in a vacuum oven for 24 h. Swelling ratio ( $S$ ) was then calculated as

$$S\% = \frac{W_2 - W_1}{W_1} \times 100$$

### Characterization

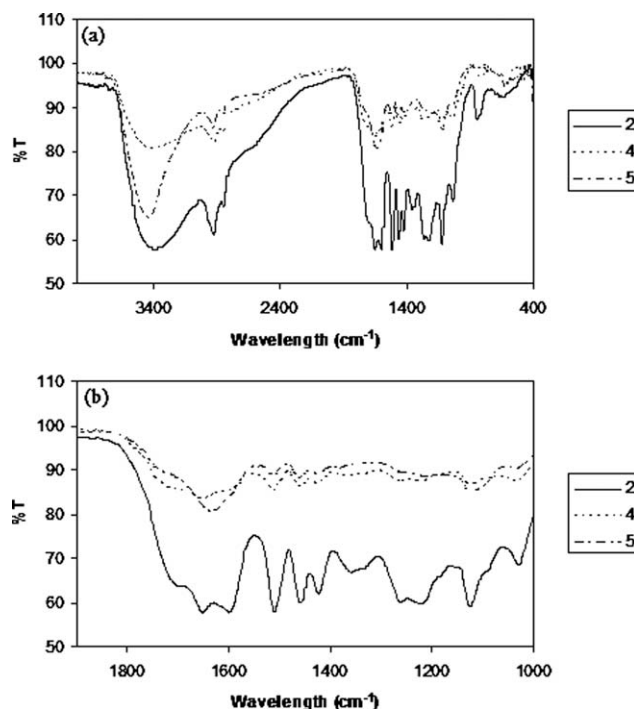
The methods of investigation were FT-IR and UV spectroscopy. FT-IR spectra were recorded on solid samples in potassium bromide (KBr) pellets by means of an FT-IR Thermo-Nicolet Model 670 Instrument (Thermo Electron, Madison, WI). The UV spectra were recorded on a Shimadzu UV-160A UV-visible recording spectrophotometer. Precipitated fractions samples (5 mg) were dissolved in dimethyl sulfoxide (DMSO; 10 mL). A 1-mL aliquot was diluted to 10 mL with DMSO, and the absorbencies between 200 and 400 nm were measured.

Scanning electron microscopy (SEM) was used to investigate the morphology of the different types of gels, i.e., radical polymerization and addition reaction crosslinked gels by using a JEOL JXA-840 A electron microprobe analyzer (JEOL USA, Peabody,

**TABLE I**  
XRF Spectrometer for the Alkaline Pulping Black Liquor

Main constituents (wt %)	Black liquor for rice straw
SiO <sub>2</sub>	14.222
TiO <sub>2</sub>	—
Al <sub>2</sub> O <sub>3</sub>	0.025
MgO	0.022
Fe <sub>2</sub> O <sub>3</sub> <sup>tot.</sup>	0.036
CuO	0.007
ZnO	0.007
ZrO <sub>2</sub>	—
CaO	0.212
Na <sub>2</sub> O	11.268
K <sub>2</sub> O	6.340
SrO	0.002
Bi <sub>2</sub> O <sub>3</sub>	0.008
RbO <sub>2</sub>	—
P <sub>2</sub> O <sub>5</sub>	0.226
SO <sub>3</sub>	0.786
I	—
Br	0.033
Cl	1.404
LOI	65.40

LOI: means lost ignition.



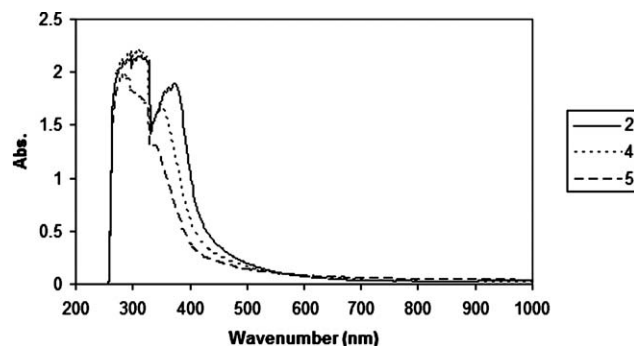
**Figure 1** FT-IR for Fractions 2, 4, and 5.

MA). The specimens for the polymer gels were frozen under liquid nitrogen, fractured, mounted, coated with gold/palladium and observed using an applied tension of 30 kV.

## RESULTS AND DISCUSSION

### Black liquor analysis

It is known that pulping is the process which reduces the lignocellulosic biomass, namely wood and agricultural residues, to a fibrous mat by separating the cellulose from the lignin. In chemical pulping, lignocellulosic residues are cooked in a “digester” at elevated pressure with a solution of the appropriate chemicals which dissolve the lignin and leave behind the cellulose. This means that the resulting liquor, called black liquor, will be rich in lignin.



**Figure 2** UV spectra for Fractions 2, 4, and 5.

**TABLE II**  
Absorbance Ratios Computed from the FTIR Spectrum  
of Lignin Samples

	$A_{3400}/A_{1500}$	$A_{1600}/A_{1500}$
Fraction 2	1.65	0.41
Fraction 4	3.26	0.86
Fraction 5	5.29	1.53

In pulping industry, a recovery for that black liquor resulting from alkaline pulping of rice straw arises with a problem due to the high silica content presents in the resulting black liquor. The analysis of the resulting black liquor shows a density of 1.0165 g cm<sup>-3</sup> and a total solid content of 4.48%.

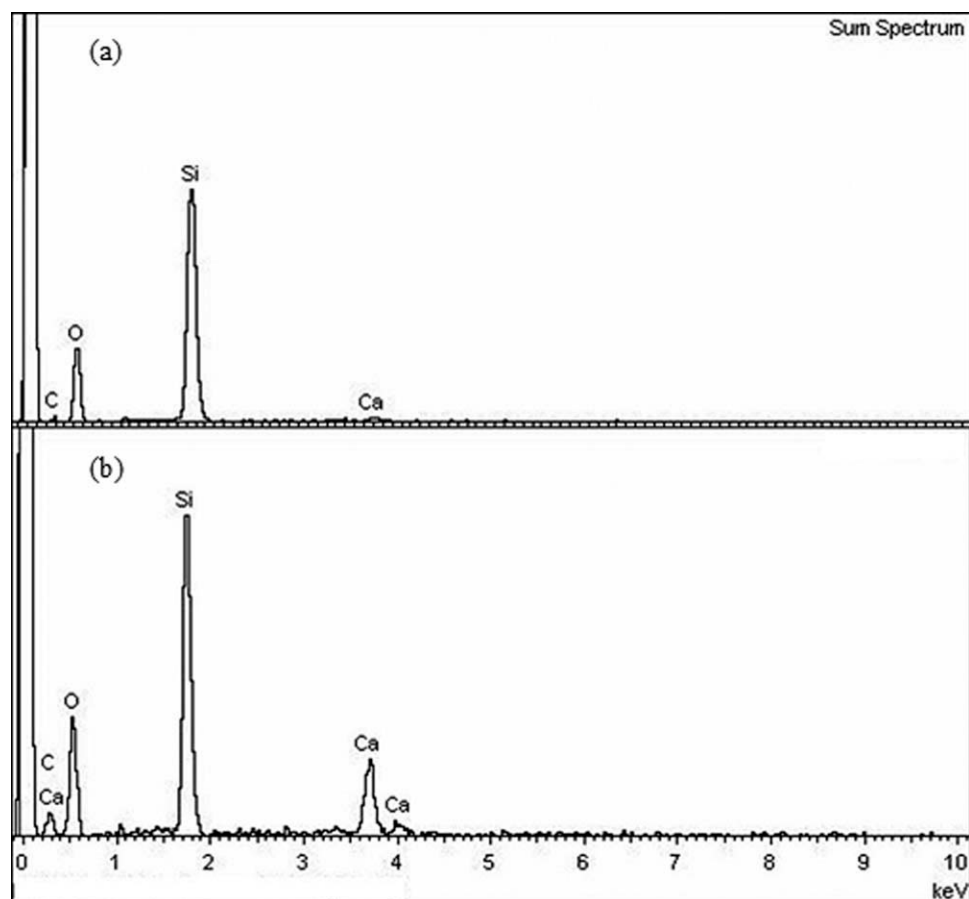
The X-ray fluorescent spectrometer (XRF) indicated the main constituents that appear in the resulting black liquor, as can be seen in Table I.

The black liquor can be considered as a complex aqueous solution, comprising organic materials from fibrous plants (lignin, polysaccharides and resinous compounds of a low molar mass) and inorganic compounds (mainly soluble salt ions). Hence, as summarized in Table I, the black liquor chemical composition affects its properties, basically those

that govern its behavior in the recovery unit. It is clear from Table I that higher silica content was noticed in the resulting black liquor resulting from alkaline pulping of rice straw which causes a problem in the evaporation during the recovery process or in using as a source of energy.

It is known from previous work,<sup>18</sup> that the lignin dissolved in the black liquor can be precipitated at pH 1.5. So, a more detailed study was carried out applying different pHs, i.e., 7.0, 4.0, 6.5, 1.5, and 5.5 again to identify the resulting precipitate which was given as a fraction numbers, where the fraction pH values can be summarized as follows: 7.0—Fraction 1; 4.0—Fraction 2; 6.5—Fraction 3; 1.5—Fraction 4; 5.5—Fraction 5. It was noticed that Fractions 2, 4, and 5 were soluble in DMSO, while Fractions 1 and 3 were insoluble. The FT-IR and UV spectra for the soluble precipitates were studied and illustrated in Figures 1(a,b) and 2.

From the FT-IR, Figure 1, one can notice that the three fractions have the same peaks with difference in intensities. The FT-IR shows the characteristic peaks for the lignin at wavelengths 1713, 1609, 1428, and 1035 cm<sup>-1</sup>. The FT-IR spectra in the region of water absorption 3000–3700 cm<sup>-1</sup>, and also



**Figure 3** EDX spectrum for (a) lignin Fraction 1 at pH 7.0 and (b) lignin Fraction 3 at pH 6.5 indicating the presence of the silica.

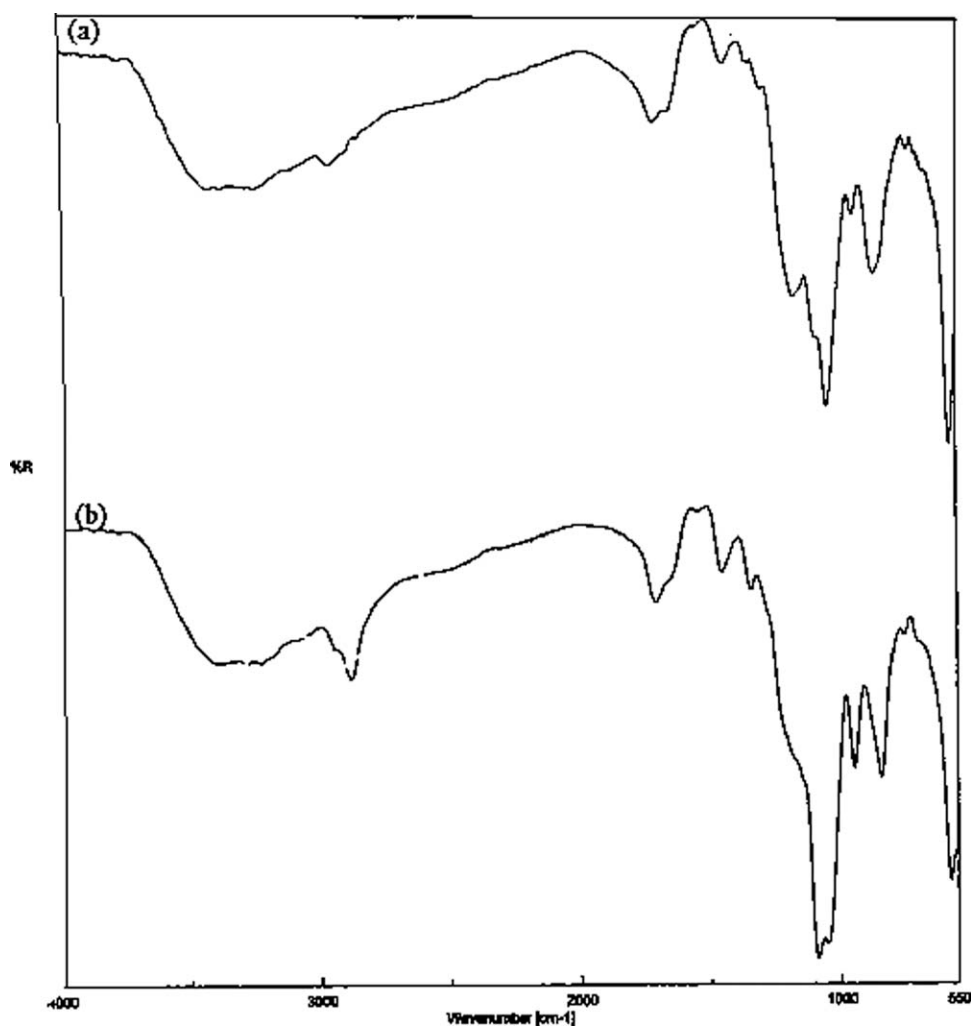


Figure 4 FT-IR for gel prepared by (a) radical polymerization reaction and (b) addition reaction.

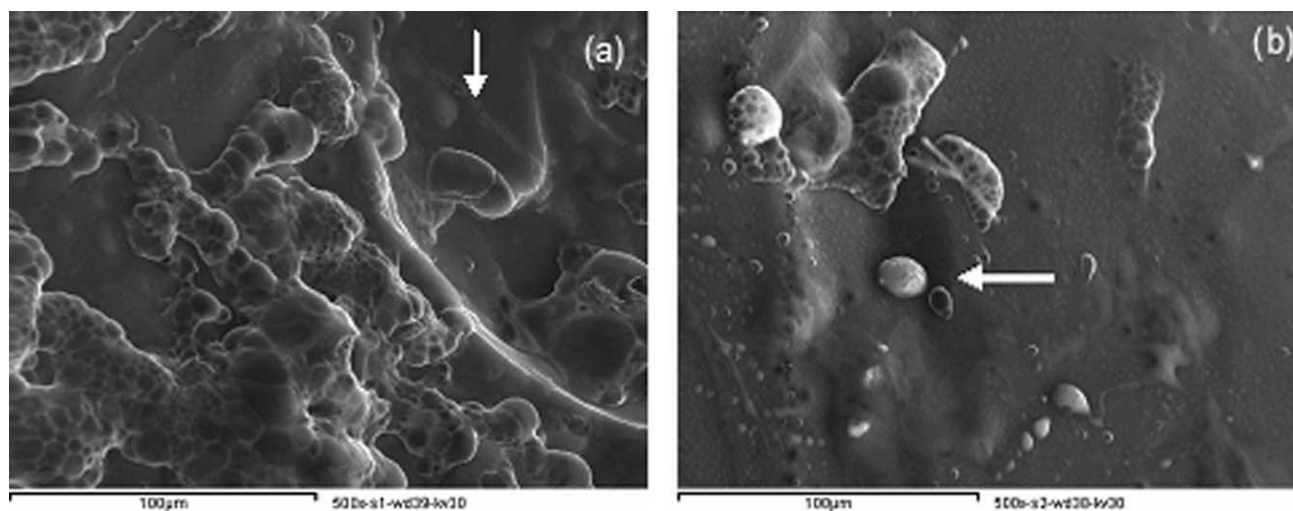
those where possible for the interactional groups  $1550\text{--}1800\text{ cm}^{-1}$  and  $900\text{--}1550\text{ cm}^{-1}$  are given in Figure 1(a,b). The absorption band centered at about  $3400\text{ cm}^{-1}$  [Fig. 1(a)] is assigned to OH groups of the water and also  $\text{—OH}$  in aliphatic and aromatic groups.<sup>19</sup> This band has approximately the same shape for the lignin obtained from agricultural plants and the peak position vary in the close limits between  $3412$  and  $3417\text{ cm}^{-1}$ .

Figure 1(b) shows the FT-IR spectra of precipitated Fractions 2, 4, and 5 from black liquor—represented only in the fingerprint region between  $1800$  and  $1100\text{ cm}^{-1}$ . This region comprises bands assigned to the main components from agricultural residues: cellulose, hemicelluloses, and lignin. Clear differences can be detected in the infrared spectra, both in the different absorbance values and shapes of the bands and in their location.

The FT-IR spectra of precipitated lignin samples [Fig. 1(b)] show the bands assigned to the characteristic bending or stretching of different specific groups of lignin in the “fingerprint” region, these

being in accordance with the literature.<sup>20</sup> There are evidenced, for example, intensities for the absorption bands specific to the carbonyl stretching ( $1716\text{ cm}^{-1}$  attributed to the nonconjugated ketone and carboxyl groups).

In the  $1550\text{--}1880\text{ cm}^{-1}$  region [Fig. 1(b)] appear many bands, that of  $1700\text{ cm}^{-1}$  being assigned to the valence vibration of the carbonyl group in ketone or carboxyl groups. This band is better evidenced in lignins from agricultural plants and in majority of woody plants appears as a shoulder. Moreover, band at  $1658\text{ cm}^{-1}$  is assigned to carbonyl stretching in conjugation with the aromatic ring, while the band at  $1713\text{ cm}^{-1}$  is attributed to carbonyl stretching in unconjugation with the aromatic ring. Aromatic ring vibrations in the lignin fractions are assigned at  $1515$ ,  $1503$ , and  $1465\text{ cm}^{-1}$ . Some shifts of the absorption bands to lower wavenumbers ( $1080\text{ cm}^{-1}$  band attributed to the aromatic C—H in plane deformation, guaiacyl-type, and C—O deformation, primary alcohol;  $1423\text{ cm}^{-1}$  band attributed to the syringyl ring breathing with CO stretching)



**Figure 5** SEM image of a black liquor hydrogel, (a) addition reaction and (b) radical polymerization reaction. The arrow indicates the presence of silica.

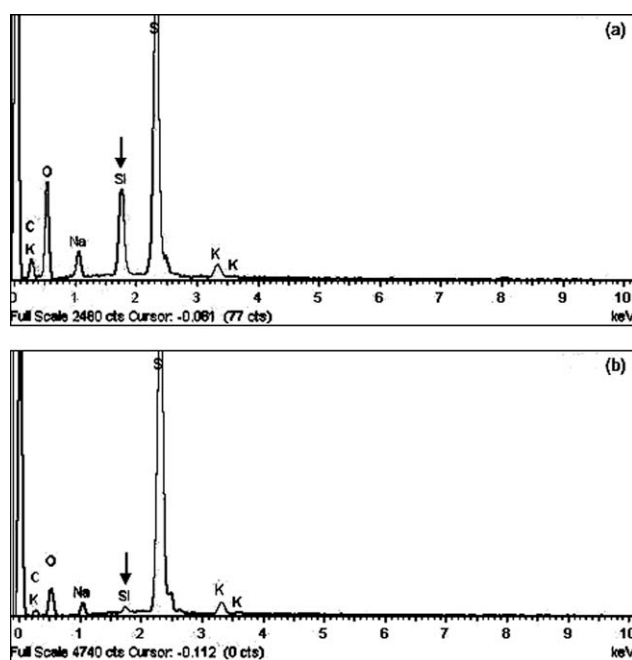
are evidenced. These are caused probably by the interactions between the functional groups.

In general, all lignin fractions show similar spectra, with the exception of the peaks intensities. Specific assignment is not easy, mainly because of the structural heterogeneity of lignin. To compare the hydroxyl contents of these samples, the maximum absorbance of the peaks at  $3400\text{ cm}^{-1}$  (O—H stretching),  $1600\text{ cm}^{-1}$  (aromatic ring vibrations peak), and  $1500\text{ cm}^{-1}$  (aromatic ring vibrations peak that can be used as internal reference)<sup>21–23</sup> were obtained and the aromatic ring substitution pattern was analyzed. The relative absorbances,  $A_{3400}/A_{1500}$  and  $A_{1600}/A_{1500}$  were then computed. The results, listed in Table II, show that Fraction 5 has a larger hydroxyl content than the other two fractions do, and therefore, in case of chemical reactions, it can more suitable to produce a derivative with a higher degree of substitution.

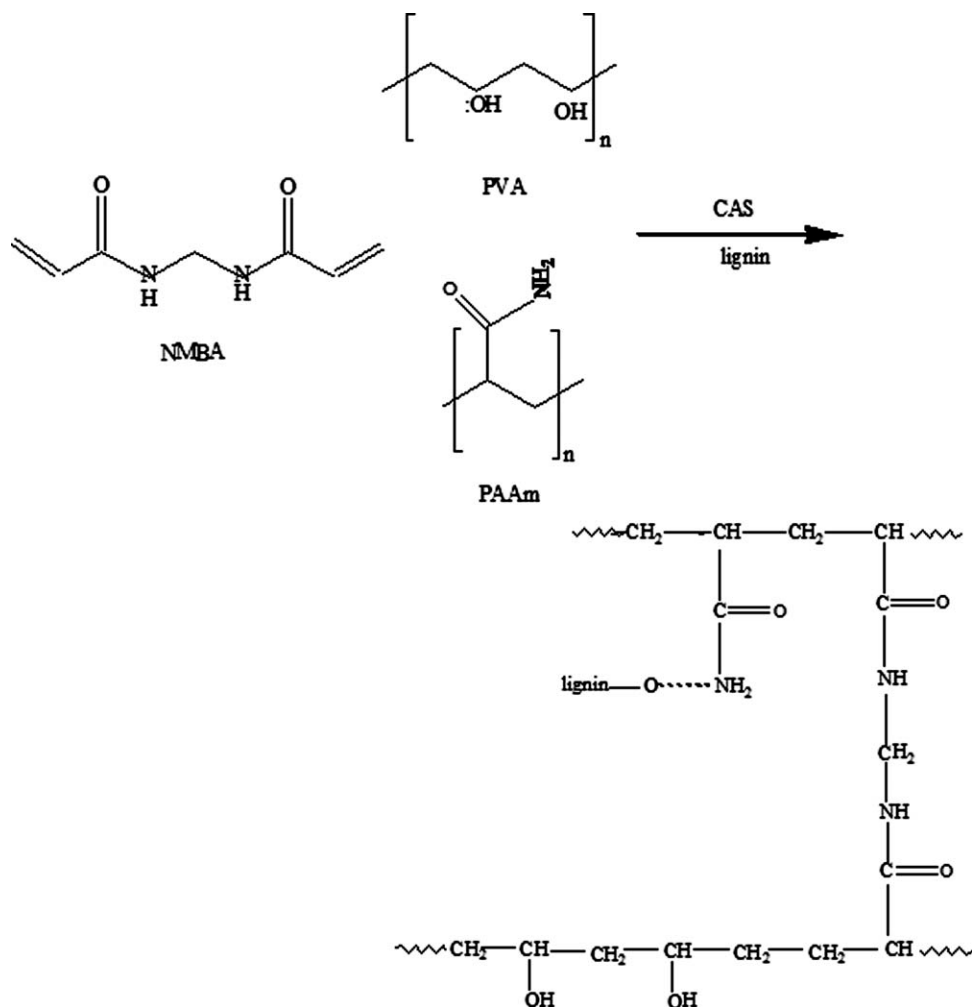
In the qualitative and quantitative UV spectroscopic determination of lignin, a typical extinction maximum at about 280 nm is mostly used. As shown in Figure 2, the three fractions exhibit the basic UV spectra typical of lignins. Absorption around 282 and 334–368 nm was observed. These results indicate that the lignin fractions were incorporated in the silica matrix. The absorption maximum at wavelength of 282 nm originates from nonconjugated phenolic groups (aromatic ring) in lignin.

On the other hand, the other two insoluble fractions precipitated at pHs 7.0 and 6.5 were characterized by SEM-EDX to identify their main constituents. The results were illustrated in Figure 3(a,b), where they indicate that only silica is present. This means that the silica can be precipitated from the black liquor at pHs 7.0 and 6.5.

The results encouraged us to try to find practical uses for the resulting black liquor to overcome its environmental water pollution. A novel hydrogel was prepared from the industrial water waste, i.e., black liquor, by graft copolymerization with PVA and PAAM to form a green polymer with a higher swelling capacity. This hydrogel was synthesized by two chemically crosslinked methods, namely radical polymerization and addition reaction. The formed hydrogels were characterized using FT-IR spectroscopy and scanning electron microscopy (SEM). The



**Figure 6** EDX image of a black liquor hydrogel, (a) addition reaction and (b) radical polymerization reaction, which represents the presence of the silica. The arrow indicates the silica.

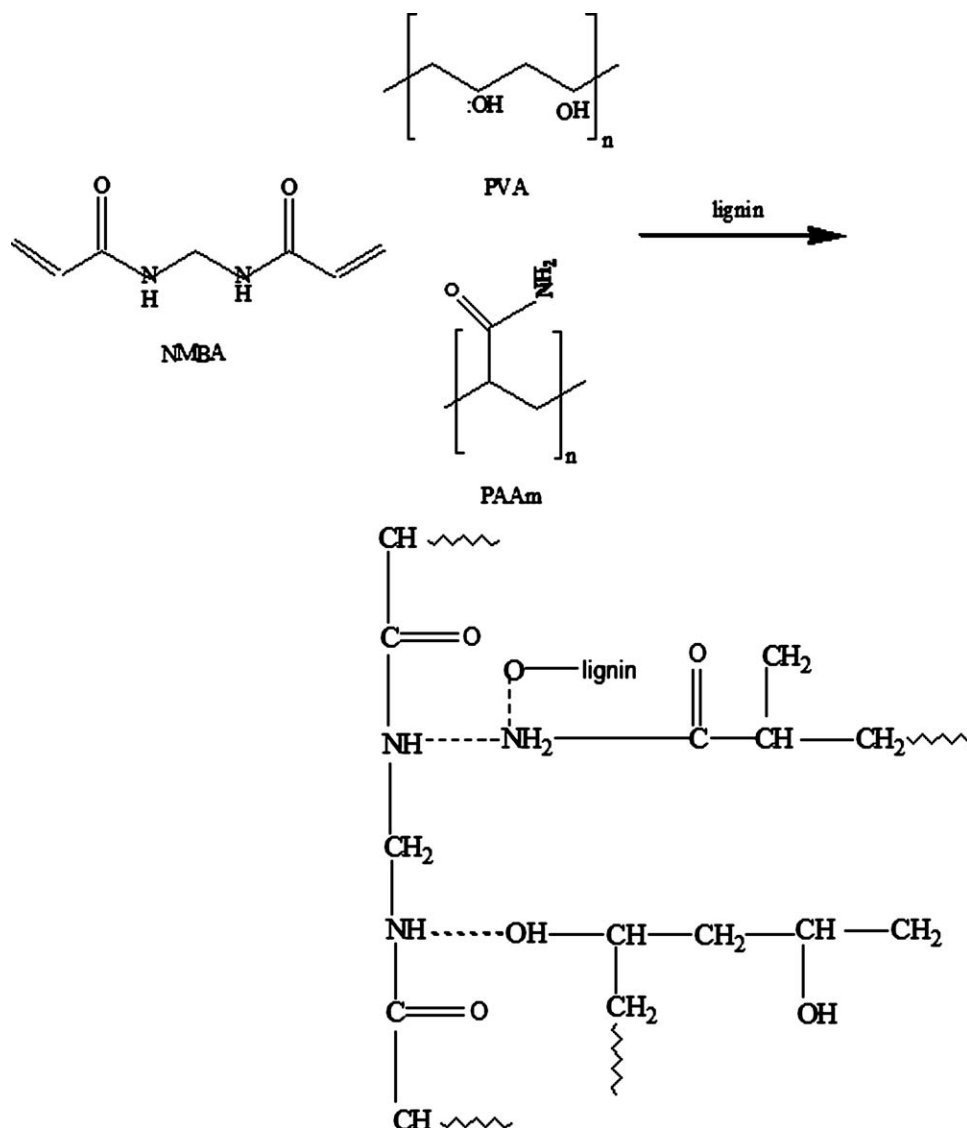


**Scheme 1** Scheme for the radical polymerization reaction.

FT-IR spectra, Figure 4(a,b), indicate a slight difference between the gels prepared via radical polymerization reaction and addition reaction. A broad band around  $3400\text{ cm}^{-1}$  in both the cases is attributed to the O—H stretching vibration of hydroxyl group of both PVA and lignin present in the black liquor. A band around  $1200\text{ cm}^{-1}$  corresponds to an acetyl group present on the PVA backbone because PVA is prepared by 80% hydrolysis of poly(vinyl acetate). The peak due to N—H stretching vibrations of the primary amide overlaps with the O—H stretching vibrations, and the aliphatic C—H stretching vibrations appeared as a small peak around  $2900\text{ cm}^{-1}$ . A characteristic peak observed around  $1700\text{ cm}^{-1}$  may be due to the carbonyl (C=O) stretching of the polyacrylamide chain in the grafted copolymer, thus confirming the grafting reaction. Further grafting was confirmed by the appearance of bands around  $1600$  and  $1460\text{ cm}^{-1}$  corresponding to an anti symmetric N—H bending and C—N stretching, respectively.

Furthermore, the changes in morphology of hydrogel samples with different reaction are illustrated in

Figure 5 for the fracture of both types of hydrogels. A sliding track is visible in Figure 5(a) for the gel resulting via addition reaction. Figure 5(b) shows a plastic surface for the gel prepared via radical polymerization. The EDX spectra, Figure 6, indicated the presence of a silica which can be found in the black liquor resulting from pulping the rice straw. Compared with the two hydrogels, it was noticed that the radically polymerized hydrogel had high swelling capacity compared to the additional reaction one. Our observation showed higher water absorption at  $25^\circ\text{C}$  for the radical polymerization crosslinked hydrogel, 60.00%, compared to the addition reaction one, 27.27%. The reason may be due to the graft polymerization mechanism that occurs during gel formation. In case of the radical polymerization crosslinked gel, the NMBA acts as a monomer to form radical ion in presence of Ce(IV). After that, the formed ion radical reacts with the co-polymer of both PVA and PAAm via a covalent bond then the lignin bonded via hydrogen bond to form the crosslinked gel, Scheme 1. The formed gel shows —NH groups beside —OH groups which can



form hydrogen bonding during the absorption of water and thus increase the swelling behavior. On the other hand, the absence of the initiator in the addition reaction led the NMBA to act as a crosslinker between the two polymers via hydrogen, Scheme 2. The formed gel will contain less free —OH group which will lead

to a decrease in the swelling behavior. Also, it was noticed that the absorption capacity depends on the temperature which shows less absorption at 50°C, 31.81% for the radical polymerization reaction and 10.52% for the addition reaction, compared to that at 25°C.

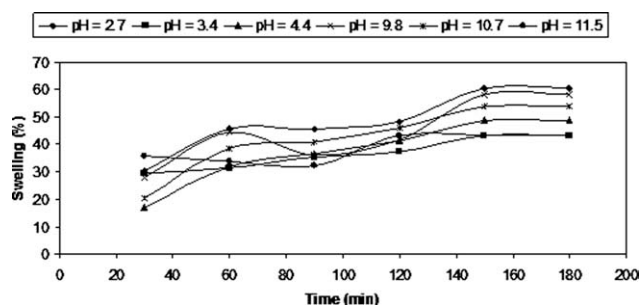


Figure 7 Swelling degree for the hydrogel prepared by addition reaction.

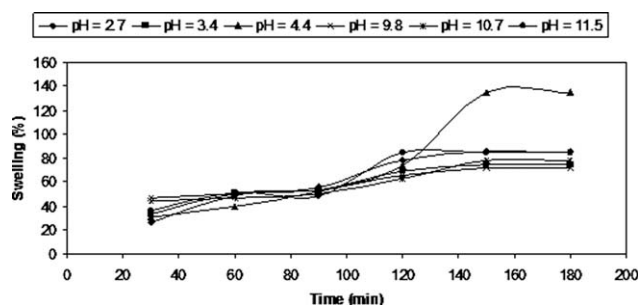


Figure 8 Swelling degree for the hydrogel prepared by radical polymerization reaction.



On the other hand, the hydrogels formed were used also to study the swelling in a solutions of different pHs. Solutions with different pHs, namely 2.7, 3.4, 4.4, 9.8, 10.7, and 11.5 were used for studying the swelling ratio of the prepared hydrogel. It was noticed that the maximum swelling was reached within 3 h as can be seen from Figures 7 and 8. The higher swelling was reached for pH 2.7 for the addition reaction hydrogel, 60.60% (Fig. 7), while it was 134.78% for the radically polymerized hydrogel for pH 4.4, Figure 8. The results also indicated that the radically polymerized hydrogel presented higher swelling ratio than that for the additionally one. Moreover, both addition and radical polymerized hydrogel show no absorption in the saline solutions which contains sodium chloride as a source of ion absorption.

### CONCLUSION

The results from this study indicated that the black liquor is considered as a complex aqueous solution. Different fractions can be precipitated according to the pH used for precipitation. The main precipitate is the lignin which is precipitated as a complex with the silica in case if using rice straw as a biomass. Using the black liquor as a source of the lignin in the preparation of hydrogel with both poly(vinyl alcohol) and polyacrylamide was investigated applying two chemical polymerization methods. The results showed that radical polymerization can occur in the presence of the initiator forming covalent bond between the cross-linker NMBA and the two polymers, while in the absence of the initiator a hydrogen bond can be formed. The results showed higher water absorption, i.e., 60.0%, at 25°C for the radical polymerization cross-linked hydrogel compared to the addition reaction one, 27.27%. Also, the hydrogel was observed to be sensitive to the pH in the absorption. Thus, one can concluded that the resulting black liquor can find an application for hydrogel preparation and thus solving

environmental water pollution that resulting from throwing it into the sea.

### References

- Hennink, W. E.; van Nostrum, C. F. *Adv Drug Deliv Rev* 2002, 54, 13.
- Bae, Y. H.; Okano, T.; Kim, S. W. *J Polym Sci B Polym Phys* 1990, 28, 923.
- Huffman, A. S.; Afrassabi, A.; Dong, L. C. *J Controlled Release* 1986, 4, 213.
- Dong, L. C.; Hoffman, A. S. *J Controlled Release* 1986, 4, 223.
- Okano, T.; Bae, Y. H.; Jacobs, H.; Kim, S. W. *J Controlled Release* 1990, 11, 255.
- Kopecek, J.; Vacik, J.; Lim, D. *J Polym Sci A-1 Polym Chem* 1971, 9, 2801.
- Alhaique, F.; Marchetti, M.; Riccieri, F. M.; Santucci, E. *J Pharm Pharmacol* 1981, 33, 413.
- Ricka, J.; Tanaka, T. *Macromolecules* 1984, 17, 2916.
- Eisenberg, S. R.; Grodzinsky, A. J. *J Membr Sci* 1984, 19, 173.
- Kwon, I. C.; Bae, Y. H.; Okano, T.; Kim, S. W. *J Controlled Release* 1991, 17, 149.
- Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *J Membr Sci* 1991, 64, 283.
- Freitas, R. F. S.; Cussler, E. L. *Chem Eng Sci* 1987, 42, 97.
- Bae, Y. H.; Okano, T.; Kim, S. W. *J Controlled Release* 1989, 9, 271.
- van Dijk-Wolthuis, W. N. E.; Franssen, O.; Talsma, H.; van Steenberg, M. J.; Kettenes-van den Bosch, J. J.; Hennink, W. E. *Macromolecules* 1995, 28, 6317.
- Stenekes, R. J. H.; Hennink, W. E. *Polymer* 2000, 41, 5563.
- Mohanty, A. K.; Misra, M.; Hinrichsed, G. *Macromol Mater Eng* 2000, 276/277, 1.
- Gould, J. M. *Biotechnol Bioeng* 1984, 26, 46.
- Ibrahim, M. M.; Agblevor, F. A.; El-Zawawy, W. K. *BioResources* 2010, 5, 397.
- Bermello, A.; Del Valle, M.; Orea, U.; Carballo, L. R. *Intern J Polym Mater* 2002, 51, 557.
- Sakakibara, A. In *Wood and Cellulosic Chemistry*; Hon, N. S., Shiraishi, N., Eds.; Marcel Dekker: New York, 1991; p 109.
- Sarkanen, K. V.; Chang, H. M.; Ericsson, B. *Tappi* 1967, 50, 572.
- Sarkanen, K. V.; Chang, H. M.; Allan, G. G. *Tappi* 1967, 50, 583.
- Fernandes, D. M.; Winkler Hechenleitner, A. A.; Job, A. E.; Radovanovic, E.; Gómez Pineda, E. A. *Polym Degrad Stab* 2006, 91, 1192.