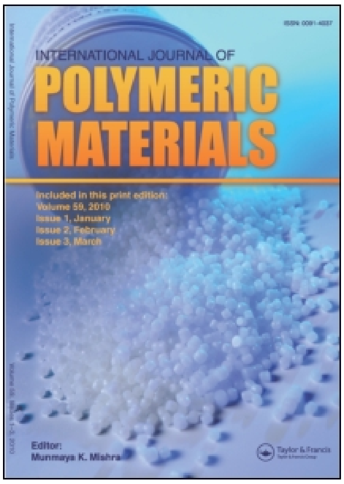


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Some aspects on the constitution of Egyptian Eichhornia crassipesphenol polycondensate resins

S. M. Sayyah[a]; A. B. Khalil[a]; M. B. Ghazy[b]
[a] Chemistry Department, Faculty of Science, Beni-Suef Branch, Cairo University, Beni-suef City, Cairo, Egypt [b] Chemistry Department, Faculty of Science, Al Azhar University, Cairo, Egypt

To cite this Article Sayyah, S. M. , Khalil, A. B. and Ghazy, M. B.(2002) 'Some aspects on the constitution of Egyptian Eichhornia crassipesphenol polycondensate resins', International Journal of Polymeric Materials, 51: 11, 981 — 1004

To link to this Article: DOI: 10.1080/714975688

URL: http://dx.doi.org/10.1080/714975688

International Journal of Polymeric Materials, 51:981–1004, 2002

0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290109804

SOME ASPECTS ON THE CONSTITUTION OF EGYPTIAN EICHHORNIA CRASSIPES–PHENOL POLYCONDENSATE RESINS

S. M. Sayyah and A. B. Khalil
Chemistry Department, Faculty of Science, Cairo University,
Beni-Suef Branch, Beni-suef City, Cairo, Egypt

M. B. Ghazy
Chemistry Department, Faculty of Science, Al Azhar University,
Cairo, Egypt

Infrared spectroscopic studies on some phenolic resins prepared by condensation of phenol with furfural, xylose, glucose, holocellulose, resistant cellulose, pure soda lignin and Egyptian Eichhornia Crassipes, were carried out. The IR spectrum of soda lignin-phenol resin proves the presence of aliphatic methyl, methylene, methine and strong bonded OH groups. Drastic changes in band position and intensity are observed in the IR spectra of pure soda lignin or Egyptian Eichhornia Crassipes and the respective phenolic resins, indicating that degradation processes could take place during the condensation reactions. The IR spectra of fractions of the Egyptian Eichhornia Crassipes–phenol resin give an insight into the complicated structure of this resin. ^{1}H-NMR and UV-spectroscopic studies confirm the IR data.

Keywords: phenol polycondensates, IR spectra, NMR spectra, UV spectra

1. INTRODUCTION

The production of linear, soluble and meltable resins from some lignocellulosic materials with phenol and bisphenol A is very important for various scientific and industrial purposes [1–14]. The IR, NMR and UV studies on the condensation products of Egyptian Eichhornia Crassipes or its different constituents (i.e., pure soda lignin, holocellulose and resistant cellulose) and its acid hydrolysate such as glucose, xylose and furfural with phenol, to the best of our knowledge were not enough investigated in the literature. Very little is known about the structure of these types of polycondensate resins. This work deals with the study of the infrared, ultraviolet, and ^{1}H-NMR spectra of the phenolic resins of Egyptian Eichhornia

---

Received 21 June 2000; in final form 24 June 2000.

Address correspondence to S. M. Sayyah, Chemistry Department, Faculty of Science, Cairo University, Beni-Suef Branch, Beni-suef City, Cairo, Egypt.

Crassipes, its constituents and its acid hydrolysate in order to give an idea about the structure of these substances.

2. EXPERIMENTAL

2.1. Materials

The raw material used was Egyptian Eichhornia Crassipes obtained from El-Gezira zone (River Nile) at Beni-Suef, Egypt.

The chemical composition of the raw material, preparation of the phenolic resins and their purification were given in our previous publication [14]. All the used chemical reagents and solvents were of extra chemically pure grade. Silica gel type G60 that contains gypsum was used for TLC experiments.

2.2. Thin Layer Chromatographic Analysis

The thickness of the stationary phase film (silica gel type G60) was adjusted to 500 μm using kirschner apparatus. The mobile phase was a binary mixture of benzene and ethanol (3 : 1 by volume). The development of the TLC plates after charging with resin samples was carried out in normal saturation system at 30°C.

2.3. Fractionation of the Prepared Egyptian Eichhornia Crassipes–Phenol Polycondensate Resin

One-gram sample of the resin, which is prepared at the optimum condition [14] was fractionated by fractional dissolution method as follows:

(1) Aluminum foils were cut into sheets of area 10 × 10 cm and coated with Egyptian Eichhornia Crassipes–phenol resin sample on only one side.
(2) The coated Al-foil was dried and rolled.
(3) Different mixtures of benzene and ethanol ranging from 10% ethanol content up to 80% are used.

In each experiment the sample is extracted in the solvent mixture for three hours at 25°C, then the solution is poured in a petri-dish and left to dry.

2.4. Spectroscopic Measurements

Infrared measurements were carried out using FT-IR1650 (PERKIN ELMER) spectrophotometer. The ^{1}H-NMR runs were carried out using Varian Gemini 200 MHz NMR spectrophotometer. The NMR-proton signals of the phenolic resins have been recorded in dimethylsulfoxide with tetramethylsilane as internal reference. The ultraviolet absorption of the phenolic resins was measured using superscan spectrophotometer at room temperature in the region 350 to 195 nm.

3. RESULTS AND DISCUSSION

3.1. The Infrared Spectroscopic Studies of Phenol–Furfural

The infrared spectrum of phenol–furfural resin is represented in Figure (1a). It shows the following characteristic bands:

(a) Characteristic bands for symmetrical valency vibration for C.O.C (strong at 806 cm^{-1}, 1041 cm^{-1} and 1164 cm^{-1}).
(b) A band at 749 cm^{-1} for CH out of plane deformation showing 1,2-disubstitution in benzene ring.
(c) A band at 1590 cm^{-1} for C=C stretching vibration in benzene ring.
(d) A band at 3117 cm^{-1} for CH stretching of aromatic.
(e) A band at 3348 cm^{-1} for weak hydrogen bonded OH groups.

Other characteristic bands and their assignments are shown in Table 1.

3.2. The Infrared Spectroscopic Studies of Phenol–Xylose and Phenol–Glucose Resins

The infrared studies on the produced resin from the condensation of phenol with xylose and glucose with an acid catalyst were carried out. The IR spectrum of phenol–xylose shows the same bands as in case of phenol–furfural but with small shift in the wave number (*cf.* Fig. 1b and Tab. 1). In case of phenol–glucose, the IR spectrum shows the following characteristic bands in addition to the bands appearing for phenol-furfural:

(a) A band at 1036 cm^{-1} for OH deformation (aliphatic OH in primary alcohol) or C—O stretching vibration (*cf.* Fig. 1c).
(b) A band at 1357 cm^{-1} for CH_2 scissoring vibration.

3.3. The Infrared Spectroscopic Studies of Phenol-Resistant Cellulose and Phenol–Holocellulose Resins

The infrared spectra of phenol-resistant cellulose and phenol–holocellulose are represented in Figures 1d and e. Their assignments are given in Table 1. The IR spectra are nearly the same except the following:

(a) Two bands appear at 965 cm^{-1} and 1021 cm^{-1} for OH out of plane bending in case of phenol–holocellulose. This band disappears in case of the resistant cellulose resin.

(b) The band that appears at 3753 cm^{-1} for OH in case of phenol–holocellulose, appears at 3516 cm^{-1} in case of phenol resistant cellulose, indicating a weak hydrogen bond for phenol–holocellulose. Other IR bands and their assignments are summarized in Table 1.

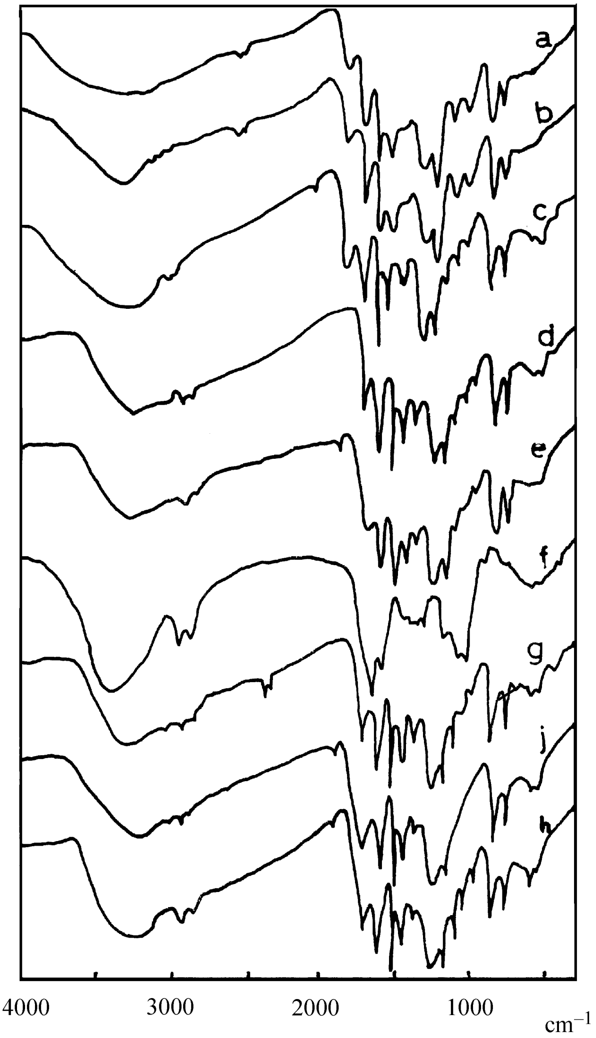


FIGURE 1 The infrared spectra of the prepared resins and different starting compound: (a) Phenol–Furfural; (b) Phenol–Xylose; (c) Phenol–Glucose; (d) Phenol–Resistant cellulose; (e) Phenol–Holocellulose; (f) Soda Lignin; (g) Phenol–Lignin; (h) Phenol–EECP; and (j) Egyptian Eichhornia Crassipes.

TABLE 1 The IR spectra assignment of different polycondensate – phenol resins

Phenol furfural	*Phenol xylose*	*Phenol glucose*	*Phenol holoce.*	*Phenol res.cel*	*Pure s.lig.*	*Phenol lignin*	*EECP*	*Phenol EECP*	*Assignment*
–	–	–	–	–	696^{ω}	730^{ω}	–	–	CH rocking vibration
749^{ω}	751^{ω}	749^{S}	753^{S}	750^{S}	750^{S}	750^{S}	–	750^{S}	CH out of plane deformation showing 1,2-disubstitution in benzene ring
806^{S}	814^{S}	832^{S}	830^{S}	833^{S}	–	–	–	833^{S}	C.O.C in furan ring
–	–	–	–	–	–	–	900^{ω}	–	1,2,3,5-tetra substitution in benzene ring
939^{S}	956^{S}	978^{S}	965^{ω}	–	–	957^{S}	968^{ω}	–	OH out of plane bending or CH rocking for CH_3
1041^{S}	1035^{S}	1000^{ω}	1021^{ω}	1098^{ω}	1022^{S}	1000^{ω}	1010^{ω}	–	C—O symmetric stretching
–	–	1036^{ω}	–	–	–	–	–	–	
–	–	–	–	–	1042^{S}	1042^{S}	1042^{S}	1042^{S}	Lignin band
1164^{S}	1159^{S}	1103^{S}	1109^{ω}	–	1122^{ω}	1104^{ω}	1109^{ω}	1105^{ω}	
–	–	1169^{S}	1168^{S}	–	–	1170^{ω}	1140^{m}	–	δ.CH aromatic and C.O.C
1225^{b}	1233^{b}	1226^{S}	1232^{b}	1225^{b}	1240^{ω}			1261^{ω}	CH wagging or CO deformation or OH carboxylic
–	1326^{ω}	1357^{S}	1361^{S}	1354^{S}	1326^{S}	1358^{S}	1326^{ω}	1363^{S}	CH Scissoring vibration for CH_3
–	–	–	–	–	1370^{ω}	–	–	–	
1418^{S}	1437^{b}	1447^{S}	1447^{S}	1449^{S}	1457^{ω}	1448^{S}	1422^{S}	1450^{S}	CH Scissoring vibration for CH_2
1506^{ω}	1510^{S}	1510^{S}	1510^{S}	1510^{S}	–	1511^{S}	–	1511^{S}	Stretching vibration of
1590^{S}	1901^{S}	1606^{S}	1601^{S}	1607^{S}	1607^{S}	1600^{S}	1638^{S}	1608^{S}	C=C aromatic
–	–	–	–	–	–	–	1675^{ω}	–	
1706^{S}	1704^{S}	1702^{S}	1699^{S}	1703^{S}	1750^{S}	–	1717^{ω}	1703^{ω}	Overtone of combination band of CH
–	–	–	–	–	–	–	1750^{ω}	–	In benzene ring and CO group
–	–					–	–	–	
2361^{ω}	2865^{ω}	–	–	–	–	–	–	2369^{ω}	Intermolecular hydrogen bond chalet
2998^{ω}	2988^{ω}	2983^{ω}	2848^{ω}	2913^{ω}	2848^{sh}	2913^{S}	2924^{ω}	2848^{ω}	
–	–	–	2923^{ω}	–	2913^{S}	–	–	2978^{ω}	CH Stretching of aliphatic
3117^{ω}	3107^{ω}	3021^{ω}	3022^{b}		3010^{ω}	3043^{ω}	3023^{ω}	3087^{ω}	

(*Continued*)

TABLE 1 (*Continued*)

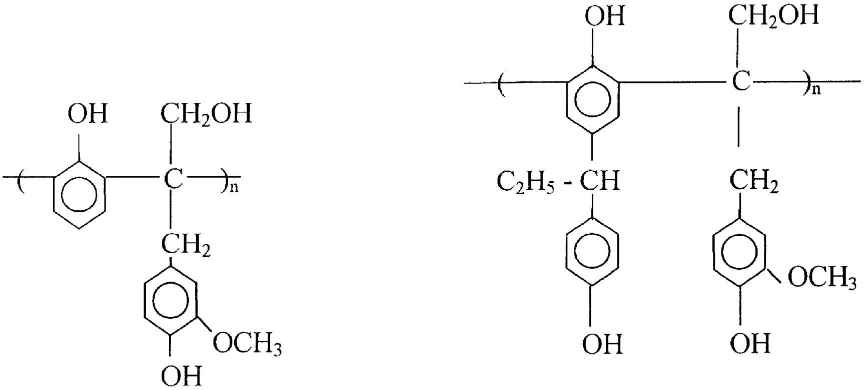
Phenol furfural	*Phenol xylose*	*Phenol glucose*	*Phenol holoce.*	*Phenol res.cel*	*Pure s.lig.*	*Phenol lignin*	*EECP*	*Phenol EECP*	*Assignment*
–	–	–	–	–	3040^{ω}	–	–	–	CH Stretching of aromatic
–	3229^{b}	3239^{b}	3295^{b}	3239^{b}	–	–	3239^{ω}	3262^{b}	Strong H bond OH group
3348^{ω}	–	–	–	–	–	3304^{b}	–	–	Medium H bond OH group
–	–	–	–	–	3402^{b}	–	3428^{b}	–	Weak H bond OH group
–	–	–	3753^{ω}	–	–	–	3750^{ω}	–	Free OH group

3.4. The Infrared Spectroscopic Studies on Soda Lignin and Phenol–Soda Lignin Resin

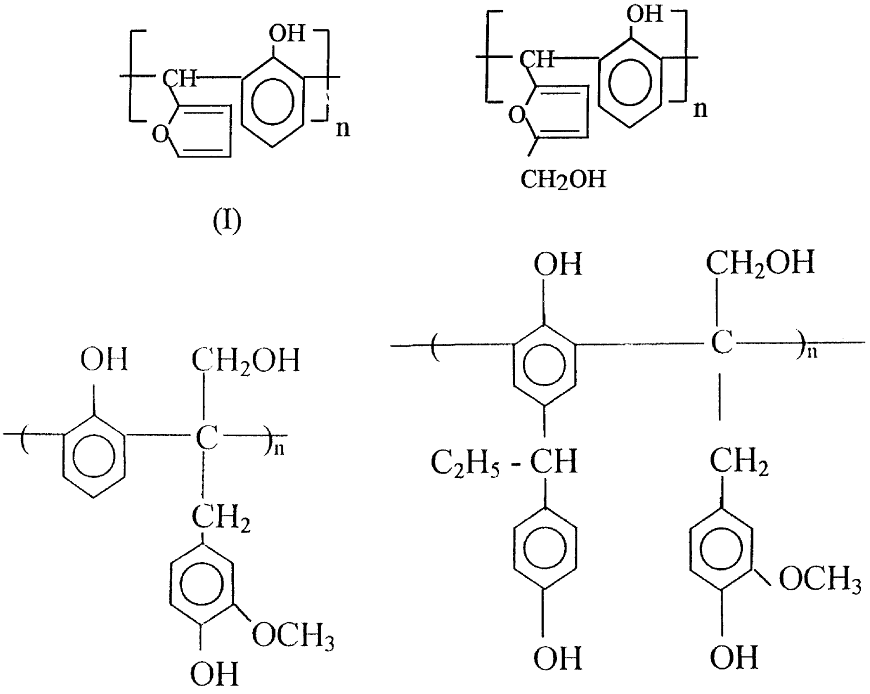
The infrared spectrum of soda lignin (*cf.* Fig. 1f) shows a broad band centered at 3402 cm^{-1}. This band includes the absorption due to the stretching vibration of strong bonded OH group. The bands within the 3000–3043 cm^{-1} region are due to the aromatic CH stretching vibrations, while these at 2913–2848 cm^{-1} are assigned to the aliphatic CH vibrations. The band appears at 1750 cm^{-1} is due to the stretching vibrations of C=O groups. The broad band appearing at 1640 cm^{-1} is due to the vibrations of the aromatic ring. The band at 1457 cm^{-1} is considered as inplane bending of the CH_3O-groups. The inplane bending of the CH_3-groups leads to the appearance of a broad split band at 1370 and 1326 cm^{-1}. The two bands appearing at 1280 cm^{-1} and 1240 cm^{-1} are assigned to the deformation vibrations of the phenolic OH groups. The other types of vibrations involving the OH group yield the absorption bands at 1174 cm^{-1} and 1122 cm^{-1}. The complex bands within the 1300–1000 cm^{-1} region would also involve some types of bending vibrations of the aromatic CH and those of the aliphatic groups. The condensation of soda lignin with phenol in acid medium resulted in a product which was purified and then investigated by infrared measurements. The spectrum (*cf.* Fig. 1g) shows new characteristic bands for CH_2 rocking vibration at 730 cm^{-1}, for CH out of plane deformation showing 1,2-disubstitution in benzene ring at 750 cm^{-1}, for CH_3 rocking vibrations at 831 cm^{-1} and 957 cm^{-1}. The broad band within 1300–1000 cm^{-1} region in case of soda lignin is resolved to several medium and sharp bands (in case of soda lignin–phenol resin) at 1000 cm^{-1} for C—O stretching vibration or OH deformation, at 1104 cm^{-1} and 1170 cm^{-1} for bending vibrations of aromatic CH, and a broad band at 1217 cm^{-1} for external deformation of CH_2 groups for deformation vibrations of OH groups [12–16]. The band, which appears at 1326 cm^{-1} for inplane bending vibration of CH_3 groups in case of soda lignin, is shifted and appears as a sharp band at 1358 cm^{-1} in case of soda lignin–phenol resin. The weak band at 1457 cm^{-1} for inplane bending of CH_3O group in case of soda lignin is shifted and appeared as a sharp band at 1448 cm^{-1} in case of soda lignin–phenol resin. On the other hand, in the 1800–1500 cm^{-1} region, the bands at 1640 cm^{-1} and 1750 cm^{-1} which appeared in case of soda lignin have disappeared in case of soda lignin–phenol resin indicating the disappearance of C=O groups. Two bands are appeared at 1511 cm^{-1} and 1605 cm^{-1} for stretching vibration of the aromatic CH groups in case of the phenolic resin. The broad band, which appeared at 3304 cm^{-1} in case of soda lignin–phenol, appeared at 3402 cm^{-1} in case of soda lignin indicating a stronger H-bonded OH group in case of soda lignin–phenol resin. The infrared studies assured the presence of aliphatic methyl, methylene, and methine groups. Also, give us an idea about the aromatic structure containing benzene ring with ortho-disubstitution and the presence of phenolic OH groups. The presence of —OCH_3 group and aliphatic OH group has been also assured. Therefore the structure of soda lignin–phenol may be one of the following two structures or both (Schemes 1 and 2), which are present in random alternation in the resin chains. This is in good agreement with the elemental analysis of the produced resin [8].

3.5. The Infrared Spectroscopic Studies on Egyptian Eichhornia Crassipes and Its Phenolic Polycondensate Resin

The spectrum of Egyptian Eichhornia Crassipes powder (*cf.* Fig. 1j) can be an overlap of the spectra of lignin and holocellulose, which can be taken as a clue for the band assignment of the infrared spectrum of Egyptian Eichhornia Crassipes powder. However, slight shifts in the position of some bands are present as well as changes in environmental interaction or overlap of bands to various degrees. Accordingly, the assignment of the infrared bands of Egyptian Eichhornia Crassipes powder and Egyptian Eichhornia Crassipes powder–phenol polycondensate resin are tabulated in Table 1 and the spectra are presented in Figure 1h. The infrared spectrum of *Egyptian* Eichhornia Crassipes powder is more complicated than that for soda lignin. In the 3750–3239 cm^{-1} region, three bands appear in the infrared spectrum of Egyptian Eichhornia Crassipes powder showing different states of OH group i.e., free OH, medium H-bond and strong H-bonded at 3750 cm^{-1}, 3428 cm^{-1} and 3239 cm^{-1} respectively. But in case



SCHEME 1



(I)

SCHEME 2

of Egyptian Eichhornia Crassipes powder–phenol resin, the bands for free and medium H-bonded OH group have vanished. Only one broad band appears at 3262 cm^{-1}, which is attributed to strong H-bonded OH group. Within the 3100–2700 cm^{-1} region, two bands appear for Egyptian Eichhornia Crassipes powder at 3087 cm^{-1} and 2924 cm^{-1} for the stretching vibrations of CH (aliphatic and aromatic) respectively. In case of the Egyptian Eichhornia Crassipes–phenol polycondensate resin, four bands appear in this region showing a weak band at 3023 cm^{-1} for asymmetric stretching vibration of CH aromatic, weak band at 2978 cm^{-1} for asymmetric stretching vibration of CH in CH_3-group, weak band at 2923 cm^{-1} for CH stretching vibration in furan ring, and weak band at 2848 cm^{-1} for CH asymmetric for CH in CH_2 group. In the 1750–1400 cm^{-1} region the bands which appeared in the infrared spectrum of Egyptian Eichhornia Crassipes powder at 1750, 1717 and 1675 cm^{-1} for C=O (acetyl linkage) and β-keto structure disappeared in the phenolic resin. The band appearing at 1638 cm^{-1} for OH (water molecules) in case of Egyptian Eichhornia Crassipes powder as a cellulosic material does not appear in case of phenolic resin. Also, the broad bands for hydroxyl groups of carboxylic acid which appeared at 1231 cm^{-1} and 1140 cm^{-1} are not observed for the phenolic resin. The two bands, which appeared at 1010 cm^{-1} and 900 cm^{-1} in the infrared spectrum of Egyptian Eichhornia Crassipes powder cellulosic material indicating C—O cellulose and 1,2,3,5-tetrasubstitution in benzene ring respectively have disappeared in case of phenolic resin. This indicates that the degradation processes of cellulosic structure of Egyptian Eichhornia Crassipes powder could take place in the strong acidic medium and that the acid hydrolysate of Egyptian Eichhornia Crassipes powder can react with phenol. Also, the disappearance of the carbonyl group bands in case of phenolic resin indicates the consumption of carbonyl groups in the condensation reaction of Egyptian Eichhornia Crassipes powder with phenol. Only one band at 1703 cm^{-1} appears as weak overtone and combination band for aromatic CH. The other bands and their assignments which appear in the infrared spectrum of the phenolic resin are outlined in Table 1. The infrared studies assured the presence of aliphatic methyl group, methylene groups, also give us an idea about the aromatic structure containing benzene ring with 1,2-disubstitution and the presence of strong bonded OH groups. The presence of O—CH_3 groups, aliphatic OH group and furan ring has also been assured. Therefore, the structure of Egyptian Eichhornia Crassipes powder–phenol resin is a contribution of the following structures, which could be present in the random alternation in the polymeric chains. This is in good agreement with the found elemental analysis of the produced resin. Also, the obtained data are in good agreement with our previous article on bagasse pith–phenol polycondensate [8, 9].

3.6. The Infrared Spectroscopic Studies on the Fractionated Products on TLC Plates

In all TLC separation processes four zones are found in the separated spots and one at the starting line. Therefore, the infrared studies on these zones were carried out in order to assess the structure of the Egyptian Eichhornia Crassipes powder–phenol polycondensate resin. It is noticed that the band intensities increase from fraction no.5 to fraction no.1 (where fraction no.1 is at the upper boundary of the spot and fraction no.5 is at the starting line). These zones may be due to different fine structures present in the resin chains or due to different molecular weights. The infrared spectra show that all absorption bands which appear in fraction no.1, also appear in the other fractions with slight shift in some cases. In fraction no.5 (i.e., the highest molecular weight zone), there are three absorption bands which appear only in this fraction at 1048 cm^{-1}, 1130 cm^{-1} and 2885 cm^{-1}, for lignin band, CH stretching in benzene ring and CH stretching vibration in methyl group, respectively. This indicates that the resin chains which may contain lignin units are in the highest molecular weight fractions (no. 4 and 5). The absorption band appearing at 3667 cm^{-1} for free OH group appears as sharp band in fraction no. 1 indicating that the free OH groups are only present in the low molecular weight fractions (*cf.* Fig. 2).

3.7. The Infrared Spectroscopic Studies on the Obtained Fraction from Fractional Dissolution Method

The infrared spectroscopic studies are performed for the fractions obtained from the fractional dissolution method. The IR spectra of the obtained eight fractions are represented in Figure 3. All bands which appear in the IR spectrum of Egyptian Eichhornia Crassipes powder–phenol resin also appear in all fractions of the resin except bands which assure the presence of methylene and methyl groups in the resin structure. These bands appeared in the high molecular weight fractions (6–8), at 608 cm^{-1}, 874 cm^{-1}, 1042 cm^{-1}, 2848 cm^{-1} and 2875 cm^{-1} which are attributed to 1,2,3,5-tetrasubstituted benzene ring, CH_3 rocking vibration, lignin band and, ν-CH stretching vibration in CH_3 group respectively, indicating that the lignin hydralysate units are concentrated in the highest molecular weight fractions (6–8). The obtained data confirm the infrared studies on the TLC fractions.

3.8. ^{1}H-NMR Spectroscopic Studies on Phenol–Furfural Resin

The ^{1}H-NMR spectrum of furfural–phenol polycondensate resin, recorded in dimethylsulfoxide as solvent, shows a pattern represented in Figure 4a. The singlet which appeared at $\delta = 2.1$ ppm may be due to the methine proton [17, 18], while the singlet $\delta = 3.5$ ppm is due to solvent protons. The multiple signals at ($\delta = 6.5-7.7$ ppm) may be attributed to the aromatic protons and furan protons. The downfield singlet signal at $\delta = 9.5$ ppm may be due to the OH group proton. The peak at $\delta = 9.0-10$ ppm disappeared after addition of D_2O which assure the presence of OH group (*cf.* Tab. 2).

3.9. ^{1}H-NMR Spectroscopic Studies on Phenol–Xylose Resin

The ^{1}H-NMR spectrum of xylose–phenol polycondensate resin is represented in Figure 4b. The δ-values and their assignments are summarized in Table 2. The singlet signal which appeared at $\delta = 2.1$ ppm may be due to the methine proton, while the singlets at $\delta = 2.5$ ppm and $\delta = 3.5$ ppm are due to solvent protons [19, 20]. The multiplet signals at ($\delta = 6.5-7.7$ ppm) may be attributed to the aromatic and furan ring protons. The downfield

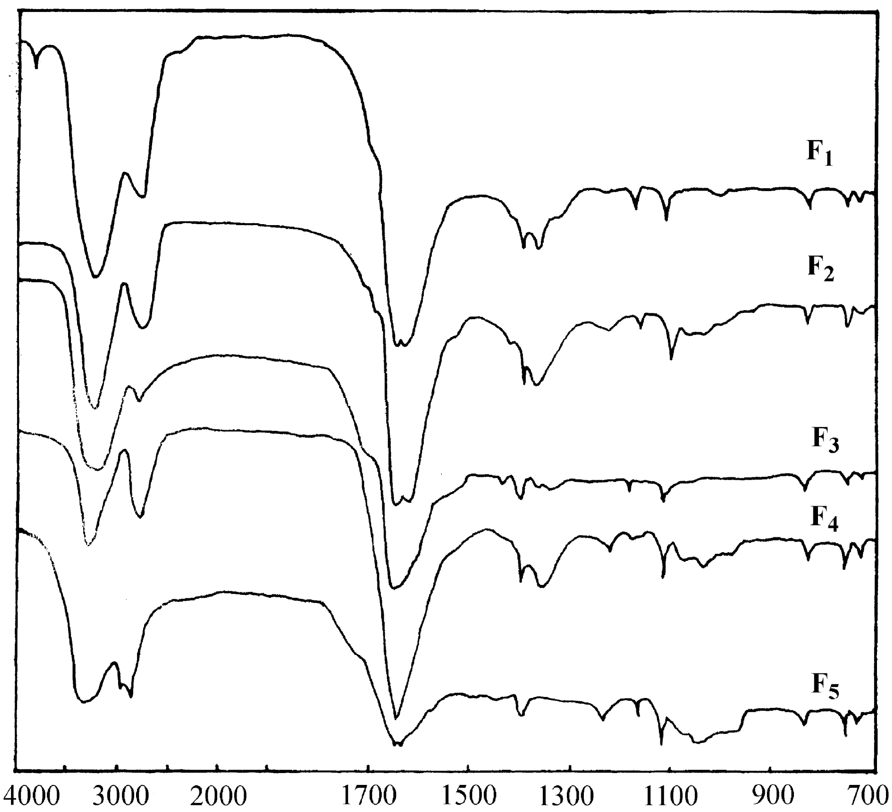


FIGURE 2 The infrared spectra of fractions collected from TLC-plates.

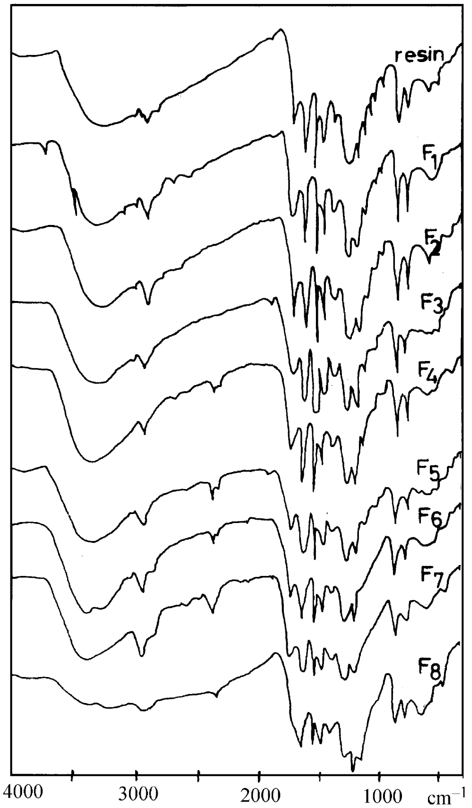


FIGURE 3 The infrared spectra bands of the unfractionated resin and fractions collected by fractional dissolution method.

singlet disappears after addition of D_2O which assure the presence of OH group.

3.10. ^{1}H-NMR Spectroscopic Studies on Phenol–Holocellulose Polycondensate Resin

The ^{1}H-NMR spectrum of holocellulose–phenol polycondensate resin is represented in Figure 4e. The proton signals and their assignment are summarized in Table 2. The spectrum shows one singlet band at $\delta = 3.00$ ppm which may be due to methine proton (CH) attached to aromatic and furan ring. The doublet signal at $\delta = 3.65$ ppm could be attributed to the methylene group proton in —CH_2OH. The singlet at $\delta = 3.285$ ppm is attributed to aliphatic OH group in —CH_2OH attached to furan ring. The other multiplet peak at $\delta = 6.5–7.7$ ppm proves the presence of aromatic

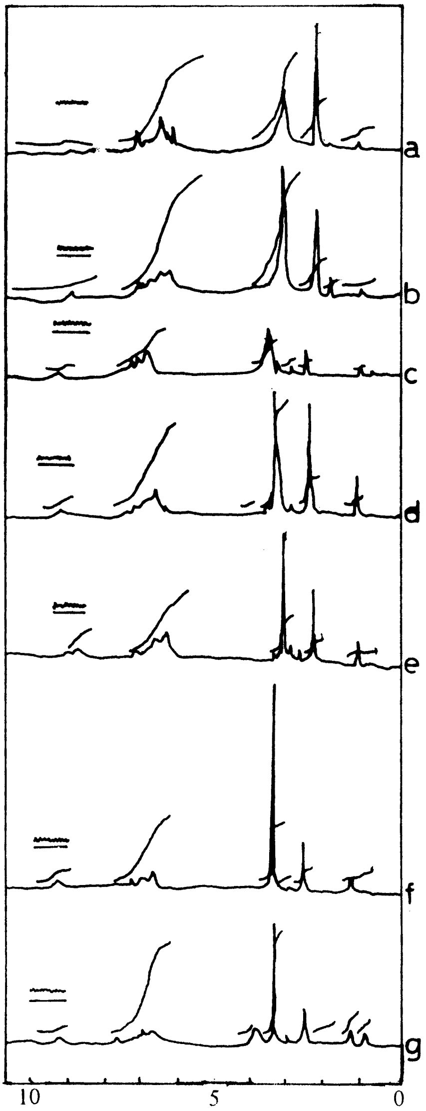


FIGURE 4 H^1-NMR spectra of different produced resins: (a) Phenol–Furfual; (b) Phenol–Xylose; (c) Phenol–Glucose; (d) Phenol–Resistant cellulose; (e) Phenol–Holocellulose; (f) Phenol–Soda lignin; and (g) Phenol–EECP.

ring and furan ring protons. The phenolic OH proton appears in the downfield as singlet at $\delta = 9.33$ ppm. Both singlets at $\delta = 3.285$ ppm and $\delta = 9.33$ ppm disappear after addition of D_2O. This proves the presences of aliphatic and aromatic OH group protons.

TABLE 2 ^{1}H-NMR spectra of different phenolic resin

Band character	*Furfural phenol*	*Xylose phenol*	*Glucose phenol*	*Res.cell. phenol*	*Holo.cell. phenol*	*Soda lig. phenol*	*EECP phenol*	*Assignments*
multiplet	–	–	–	–	–	–	1.2–1.4	For CH_2 or CH–Et group protons
singlet	2.1	2.1	–	–	–	–	–	Methine proton
singlet	2.5	2.5	2.5	2.5	2.5	2.5	2.5	Solvent proton
singlet	–	–	2.968	3.0	3.0	3.0	3.0	Methine proton
singlet	–	–	–	3.285	3.3	–	–	Aliphatic OH protons
singlet	–	–	–	–	–	3.3	–	For OCH_3 group
singlet	3.5	3.5	–	3.5	3.5	–	3.5	Solvent protons
singlet	–	–	3.0–3.6	–	–	–	–	Overlap of solvent protons signal and doublet of CH_2OH group and singlet for OH
multiplet	–	–	–	–	–	3.4–3.7	–	Overlap of solvent protons signal and $CH_2CH_2OH_2OCH_3$ and aliphatic OH group
doublet	–	–	–	3.65	3.6	–	3.6	CH_2, CH groups
doublet	–	–	–	–	–	–	4.2	OH group in CH_2OH
multiplet	6.5–7.7	6.5–7.7	6.5–7.7	6.5–7.7	6.5–7.7	6.5–7.7	6.5–7.7	Overlap of benzene and furan rings protons
multiplet	9–10	9–10	9–10	9–10	9–10	9–10	9–10	Phenolic OH

3.11. ^{1}H-NMR Spectroscopic Studies on Phenol–Soda Lignin Polycondensate Resin

The ^{1}H-NMR spectrum of soda lignin–phenol polycondensate resin is represented in Figure 4f. The proton signals and their assignments are given in Table 2. The spectrum shows one multiple peak at $\delta = 3.4-3.7$ ppm which may be due to the protons of O—CH_3, CH and CH_2 groups. From the literature [19, 20], the protons of O—CH_3 group appear as singlet at 3.6 ppm. Therefore, the presence of CH, CH_2, O—CH_3 and aliphatic OH groups in the resin structure leads to the multiplet signal appearing at $\delta = 3.4-3.7$ ppm. The other multiplet peak at $\delta = 6.5-7.7$ ppm may be attributed to the aromatic and phenolic protons. The singlet at $\delta = 9-10$ ppm is attributed to the phenolic OH protons. The peaks appearing in this region disappear after addition of D_2O to the resin sample, which assure the presence of OH groups.

3.12. ^{1}H-NMR Spectroscopic Studies on Phenol–Egyptian Eichhornia Crassipes Powder Polycondensate Resin

The proton NMR spectrum of Egyptian Eichhornia Crassipes–phenol polycondensate resin using dimethylsulfoxide as a solvent is represented in Figure 4g. The proton signals and their assignment are given in Table 2. The spectrum shows one multiplet peak at $\delta = 3.6$ ppm which could be attributed to the presence of O—CH_3, CH, CH_2 and aliphatic OH protons. The phenolic OH protons show a singlet at $\delta = 9.33$ ppm. The multiplet peak at $\delta = 6.5-7.7$ ppm may be due to the aromatic ring and furan ring protons. So, the complicated spectrum of Egyptian Eichhornia Crassipes powder–phenol resin indicates that the structure includes lignin hydrolysate units, furan rings and phenolic OH groups in a complicated aromatic structure (*cf.* Scheme 2).

3.13. Ultraviolet Spectroscopic Studies on Different Resins [18, 19]

The benzene chromophore has three absorption bands at 184 nm for the $\pi-\pi*$ allowed transition, and at 204 nm and 256 nm for $\pi-\pi*$ forbidden transition in highly symmetrical benzene molecules. Substitution on the benzene ring of auxochromic groups like OH shifts the E_2 and β-bands to longer wavelength, frequently with intensification of the β-band and loss of its fine structure because of $n-\pi$ conjugation. Phenol has two main bands in the ultraviolet region at 211 nm due to E-band ($A_{1g} \rightarrow \beta_{1u}$) and at 270 nm due to β-band ($A_{1g} \rightarrow \beta_{2u}$). Substitution should also primarily exhibit red shift and intensification of the longitudinally polarized band [21, 22]. The ultraviolet spectra of the phenolic resins under investigation are represented

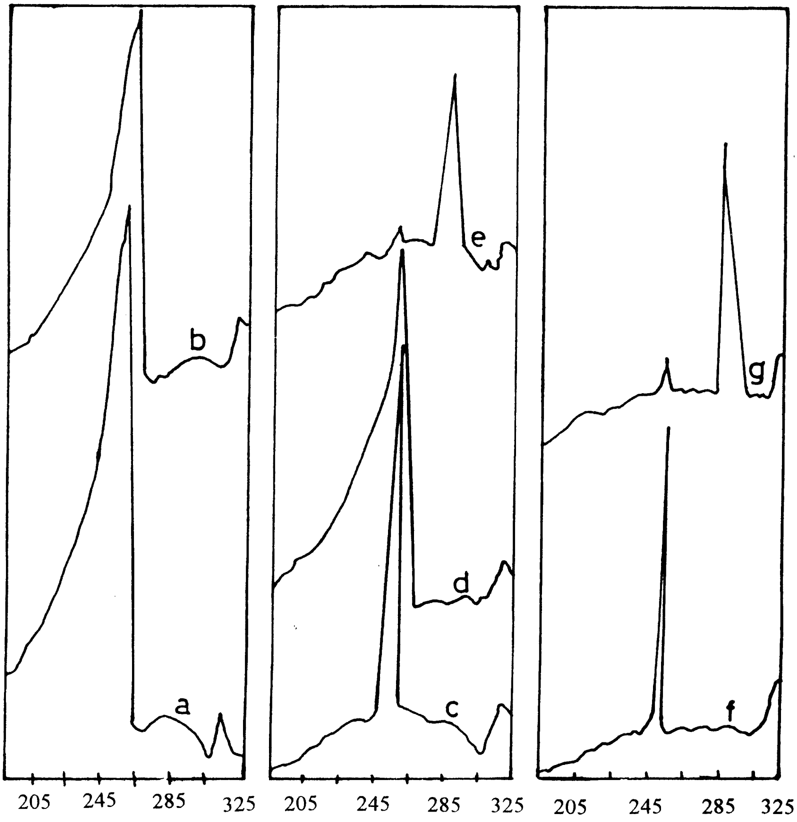


FIGURE 5 The ultraviolet spectra of the different produced resin samples: (a) Phenol–Furfual; (b) Phenol–Xylose; (c) Phenol–Holocellulose; (d) Phenol–Resistant cellulose; (e) Phenol–Soda lignin; (f) Phenol–Glucose; and (g) Phenol–EECP.

in Figure 5 and the maximum absorption band (λ_{max}) and their assignment are given in Table 3.

The UV-spectrum of furfural–phenol resin shows absorption bands at 199, 209, 255, 259 and 283 nm, which may be due to $\pi-\pi*$ transition of the β-band (phenolic and furan ring). The last absorption band at 315 nm may be due to $n-\pi*$ transition of the substituted furan ring. The presence of an ortho-disubstituted phenolic moiety leads to bathochromic shifts as shown in Figure 5a.

The UV spectrum of resistant cellulose–phenol resin shows absorption bands at 307 and 321 nm, which may be due to $n-\pi*$ transition for the substituted furan ring in position four by the CH_2OH group [23].

TABLE 3 UV-absorption bands of different phenolic polycondensate resins and their assignments

Furfural phenol	*Xylose phenol*	*Glucose phenol*	*res.cell. phenol*	*holo.cell. phenol*	*soda lig. phenol*	*EECP phenol*	*Assignments*
199	199	191	189	195	195	195	$\pi-\pi*$ transition (E_2 band) in furan and benzene ring
209	–	201	201	205	205	207	
–	–	–	211	–	–	213	
–	–	–	219	215	215	–	
–	–	–	–	221	221	225	
–	–	231	230	239	239	237	
–	245	–	–	–	–	–	
255	–	–	–	–	–	–	
259	–	–	259	257	257	257	
–	261	261	–	–	–	261	
–	269	–	269	267	267	269	$\pi-\pi*$ transition of phenolic system or β-band A_{1g}-$\beta_2\mu$
–	277	–	–	–	–	279	
283	–	283	289	283	283	289	
–	–	–	–	291	291	–	
–	299	297	–	–	–	299	$\eta-\pi*$ transition of substituted furan ring
–	301	–	–	–	–	301	
–	–	307	–	310	310	307	
315	317	319	317	317	317	317	
–	–	–	–	–	–	320	

The UV spectrum of holocellulose–phenol shows the characteristic absorption bands for trisubstituted benzene ring and monosubstituted furan ring system (1-position) at 219, 230, 259, 269 and 289 nm. The appearance of the absorption band at 317 nm may prove the presence of mono- and disubstituted furan ring (1,4-position), and this may be due to $n-\pi*$ transition. Due to the presence of complicated aromatic system in case of soda lignin–phenol resin, a broad absorption band appeared with $\lambda_{max.}$ centered at 283 nm with small shoulders in the right and left side. The UV spectrum shows absorption bands at 195, 205, 215, 221, 239, 252, 267 and 283 nm, which may be due to $\pi-\pi*$ transition of the complicated aromatic system. The two absorption bands at 310 and 317 nm, which may be due to $n-\pi*$ transition of the phenolic moiety substituted with O—CH$_3$ group in *m*-position and *p*-substitution with —CH and C$_2$H$_5$ groups, also may be due to

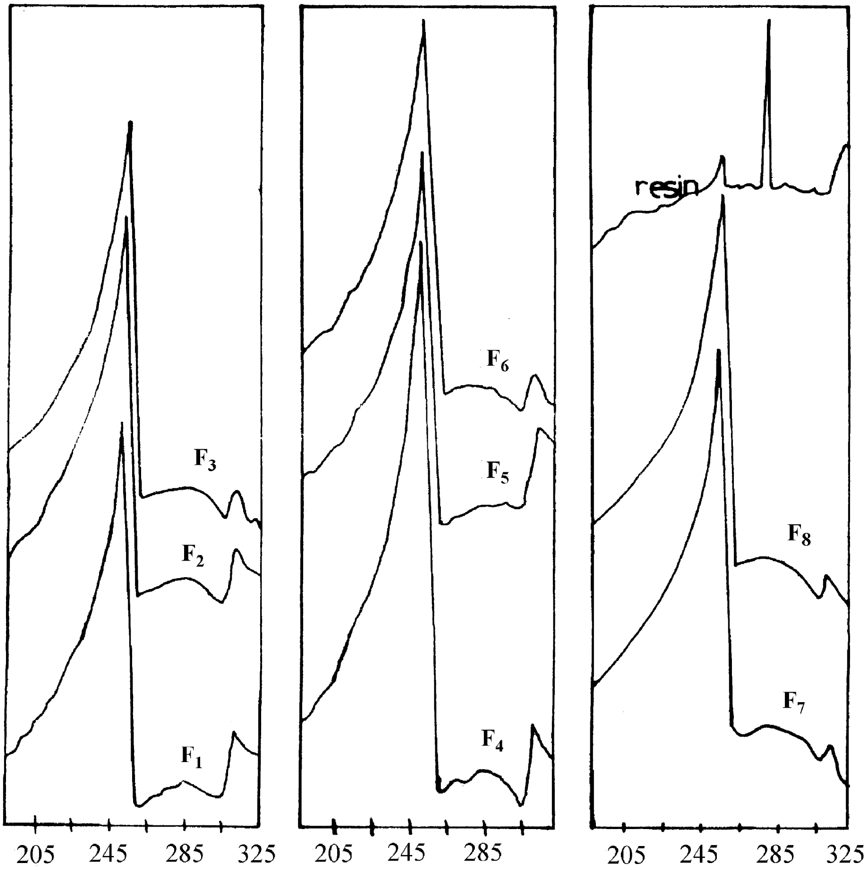


FIGURE 6 The ultraviolet spectra of the fractions collected from fractional dissolution method and unfractionated resin.

the ortho-disubstituted phenolic ring. The maximum absorption of each band is given in Table 3. The UV spectrum is represented in Figure 5. The UV spectrum of Egyptian Eichhornia Crassipes–phenol polycondensate resin is represented in Figure 5. The spectrum shows different absorption bands at 195, 207, 213, 225, 237, 257, 261, 269, 279, 289, 299, 301, 307, 317 and 321 nm. From the above observations it is clear that the structure of the phenolic resin of Egyptian Eichhornia Crassipes is a contribution of lignin and holocellulose hydrolysis products with phenol in the resin chains. The assignments of the UV absorption bands are given in Table 3.

3.14. Ultraviolet Spectroscopic Studies on Fractions Obtained by Fractional Dissolution Method

The UV spectra of the obtained fractions are represented in Figure 6. The absorption band at 195 nm in case of unfractionated resin can be detected in

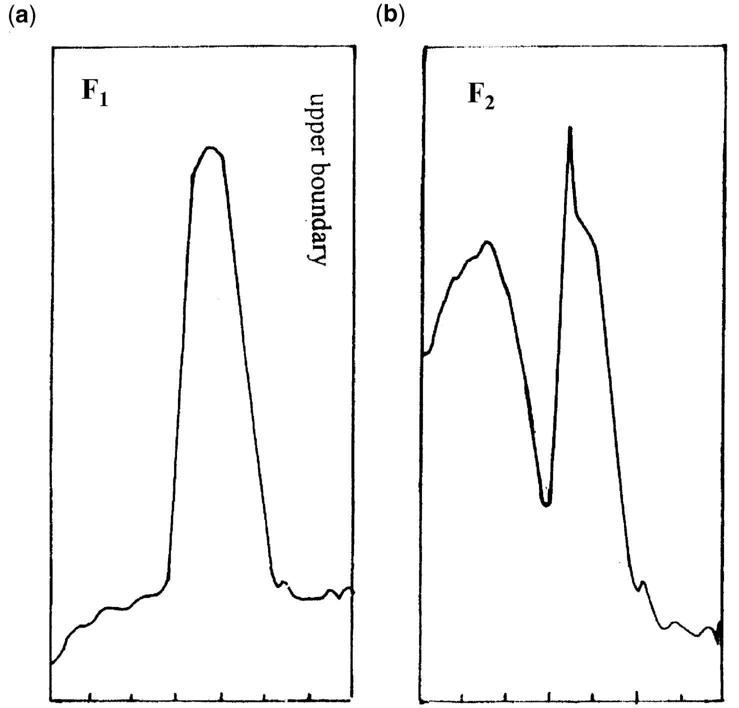


FIGURE 7 The ultraviolet spectra of the fractions collected from TLC-plates and unfractionated resin. (*Continued*)

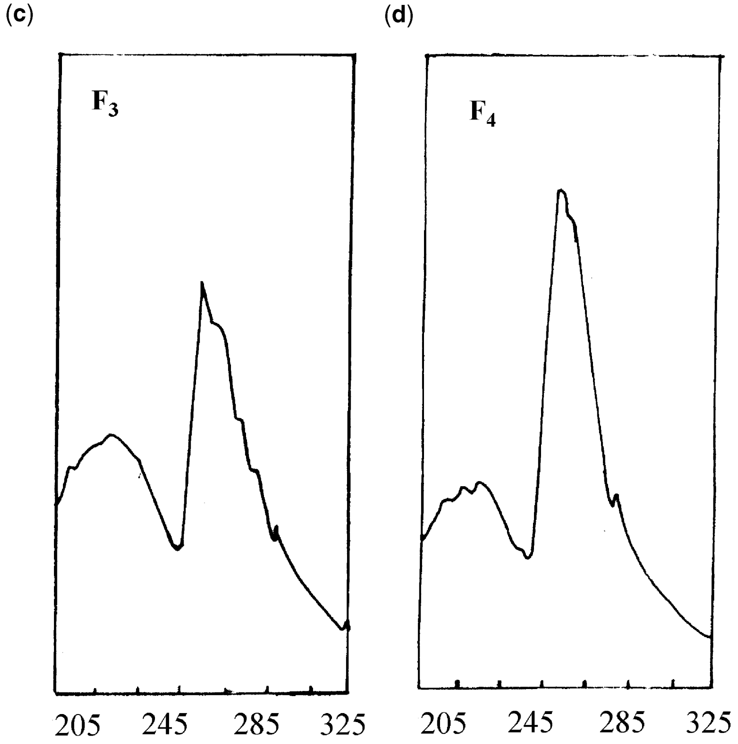


FIGURE 7 (*Continued*)

fraction no. 2, 4 and 6 while the band appears at 205 nm in the unfractionated resin can be detected in fraction no. 1, 3 and 5. While the absorption band at 213 nm in the unfractionated resin appears in all fractions, but with slight shift except fraction no. 8. However the absorption band appears at 225 nm in the unfractionated resin appears only in fraction number 7 at 221 nm. The absorption bands appearing at 257, 269, 279 and 289 in case of the unfractionated resin appear also in case of the resin fractions, but with slight shift. The absorption band appearing at 307 nm in the unfractionated resin appears in case of all resin fractions at 311 nm. The absorption band that appears in the unfractionated resin at 321 nm appears only in case of fraction no. 3, 5 and 6. The UV spectra of all fractions are approximately the same. There are no drastic changes in the UV spectra of the fractions obtained by the fractional dissolution method. This means that the fractionation is not efficient to separate different fine structures present in the different polymeric chains. The separation on TLC-plates is more efficient and gives a precise and good idea about the complicated structure of the Egyptian Eichhornia Crassipes phenol resin.

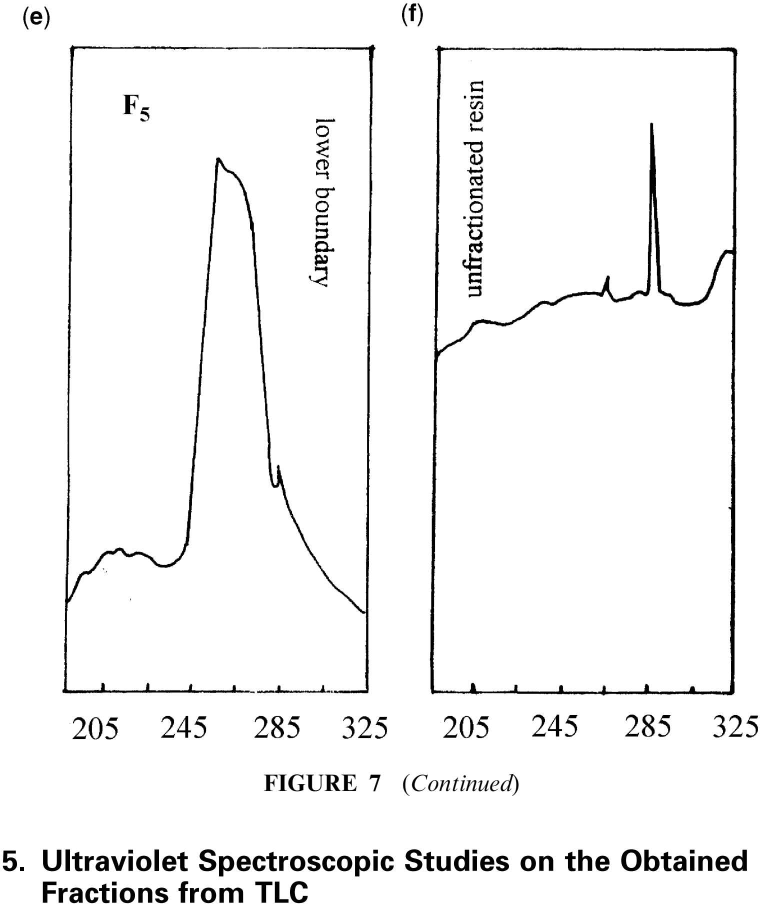


FIGURE 7 (*Continued*)

3.15. Ultraviolet Spectroscopic Studies on the Obtained Fractions from TLC

The zones which appear on the chromatoplates in case of TLC-separation of Egyptian Eichhornia Crassipes – phenol polycondensate resin led us to conduct further studies on these zones. The UV investigations on these fractions were performed from 185 – 325 nm. It is noticed that the absorption band, which appears at 213 nm in the unfractionated resin, appears at 209 nm in fraction no.1 (upper zone i.e., low molecular weight fraction), at 211 nm as a broad band in fraction no.2, 3, 4 and 5. Also the three absorption bands, which appear at 225, 257 and 269 nm in case of unfractionated resin, appear as two absorption bands at 225 and 261 nm in case of fraction no.1. But, in case of fraction no.2, three absorption bands appear at 221, 249 and 259 nm. In fraction no.3, three absorption bands appear at 227, 253 and 263 nm. However, in case of the last two fractions, four bands appear at 227, 235, 253 and 257 nm in fraction no.4, but three absorption bands appear at 225, 253 and 259 nm in case of fraction no.5. The absorption bands, which appear at 279 and 289 nm in case of unfractionated resin also, appear in case of fraction no.1, 2 and 3. Only one absorption band in case of the last two fractions (4 and 5) is detected at 285 nm. The absorption band at 299 nm in case of unfractionated resin appears also in fractions number 1 and 2 but does not appear in fractions number 3, 4 and 5. The last three absorption bands at 307, 317 and 321 nm in case of unfractionated resin appear in fractions number 1 and 2 as two absorption bands at 305 and 320 nm. But only one absorption band appears in case of fractions number 3 and 4 at 319 nm and 315 respectively and no peaks are traced in fraction number 5. From the above description of the UV spectra of the separated fractions on TLC-plates and the unfractionated one, it is clear that the Egyptian Eichhornia Crassipes–phenol resin has a complicated structure and the different fractions or zones which appear on the TLC – plates have different structures (i.e., fine structure) but have the same functional groups. Consequently, the appearance of these zones on the TLC-plates can be due to the presence of different structures. On the other hand, one can conclude that substituted furan rings are present in the light resin fractions, but the complicated aromatic lignin structure is present in the three heavy fractions (i.e., high molecular weight fraction).

4. CONCLUSION

The combined technique of TLC with IR and UV spectroscopic analysis gives good information about the complicated structure of Egyptian Eichhornia Crassipes–phenol polycondensate resin. The structure of this resin is an alternation of the holocellulose and lignin–hydrolysate products with phenol in the resin chains. The proton NMR spectroscopic studies confirm the data obtained from IR and UV spectroscopic analysis.

REFERENCES

[1] Kawashima, M. (1974). *Japan Pat. 7471, 118 (c1, 28D19, 28D11, 28BO), Chem. Abstr.*, **82**, 4545OF (1975).

[2] Zhdanova, R. S., Sokolova, A. A. and Kochergin, V. M. (1974). *Khim. Ispolz. Lignina*, p. 428.

[3] Lindstrom, T., Soremark, C. and Westman, L. (1977). *J. Appl. Polymer Sci.*, **21**, 2873.

[4] Vorm, A. G. and Lucius, M. (1956). *Brit. Pat. 761, 751*, Nov., 21, *Chem. Abstr.*, **51**, 7765d (1957).

[5] Bogomolov, B. D., Sokolova, A. A., Krupkina, F. A., Prosyanik, G. V., Danileskaya, R. G., Brodsii, G. S. and Zhanova, R. S. (1960). *USSR pat. 131, 459*, Sept., 10.

[6] Apil, A. and Rupp, N. (1954). *Ger. Pat. 914, 432*, July, 1 (cl.39c, 2); *Chem. Abstr.*, **52**, 11424a (1958).

[7] Moustafa, A. B., Sayyah, S. M., Gawish, N. M. and Mourad, A. A. (1984). *Egypt J. Chem.*, **27**, 737.

[8] Saad, S. M., Sayyah, S. M., Metwally, N. E. and Mourad, A. A. (1988). *Acta Polymerica*, **39**, 568.

[9] Sayyah, S. M., Saad, S. M., Metwally, N. E. and Shaaban, S. M. (1988). *Acta Polymerica*, **39**(10), 574.

[10] Sayyah, S. M., Saad, S. M. and Elwy, E. (1989). *Acta Polymerica*, **40**(10), 667.

[11] Sayyah, S. M., Saad, S. M. and Elwy, E. (1990). *Acta Polymerica*, **41**(1), 63.

[12] Sabbah, I. A., Khalifa, F. A., Metwally, N. E. and Sayyah, S. M. (1992). *Egypt J. Chem.*, No. 6, 651.

[13] Sayyah, S. M., Rashed, Z. H., Shemeiss, N. A. M. M., Farrag, A. E. and Ghazy, M. B. (1997). *Egypt. J. Chem.*, **40**(3), 211.

[14] Sayyah, S. M., Abd El-Khalek, A. A., Hassouna, M. E., Sabbah, I. A. and Khaliel, A. B. (1997). *Egypt J. Chem.*, **40**(5), 411.

[15] Zhbankov, R. G. (1966). *Infrared Spectra of Cellulose and its Derivatives*, New York, Consultants Bureau.

[16] Alpert, N. L., Keiser, W. E. and Szymansk, H. A. (1973). *Theory and Practice of Infrared Spectroscopy*, New York.

[17] Bovey, F. A. (1972). High Resolution NMR of Macromolecules, New York, Academic Press.

[18] Bovey, F. A. (1971). *Progr. Polymer Sci.*, **3**, 1.

[19] Gunther, H. (1980). *NMR Spectroscopy*, *An Introduction*, New York, Wiley, pp. 21–160.

[20] Young, R. I. (1981). *Introduction to Polymers*, London, Chapman and Hall, p. 140.

[21] Silverstein, R. M., Bassler, C. G. and Morill, T. C. (1974). *Spectroscopic Identification of Organic Compounds*, New York, Wiley.

[22] Scott, A. L. (1964). Interpretation of Ultraviolet Spectra of Natural Products, New York, Pergamon Press.

[23] Jaffe, H. H. and Orchin, M. (1965). *Theory and Applications of UV-Spectroscopy*, London, Wiley, pp. 305–381.