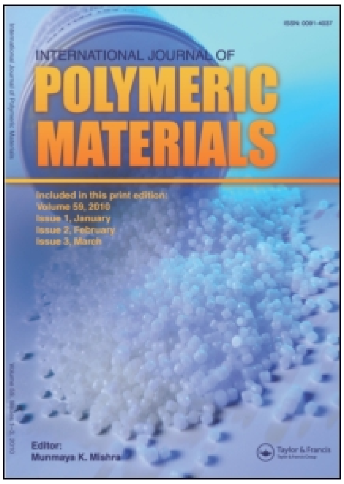

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Electrical conductivity studies on impregnated paper sheet with Eichhornia Crassipes phenol polycondensate resins

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ELECTRICAL CONDUCTIVITY STUDIES ON IMPREGNATED PAPER SHEET WITH EICHHORNIA CRASSIPES PHENOL POLYCONDENSATE RESINS

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Polycondensate resin was prepared from Egyptian Eichhornia Crassipes powder (EECP) and phenol using conc. HCl as catalyst at 100°C. Modifications of the produced resin with phenol–formaldehyde and phenol–benzaldehyde were performed. Infrared spectroscopic studies and element analysis were carried out in order to determine the complicated resin structure.

The d.c electrial resistivity (ϱ) of these materials was measured. It was found that ϱ increases with the temperature (T), together with the resin concentration (c). A maximum in ϱ was found for all samples varied from $\varrho = 10^5$ to $10^9 \Omega \cdot cm$ in the temperature range from room temperature upto 100°C.

The resistivity of the filter paper sheet was found to increase when impregnated with the resin EECP–phenol in a similar way with T and c. ϱ was found to increase more when the resin was modified with phenol–formaldehyde and less so when the resin was modified with phenol–benzaldehyde.

The data obtained for ϱ was explained in relation to both the temperature and the structure. An attempt was made to interpret the conduction mechanism in view of current theories.

Keywords: phenol polycondensates, composites, electrical conductivity

1. INTRODUCTION

The production of phenolic resins from wood lignin and other cellulosic materials was studied by earlier workers [1, 2]. Preparation and

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characterization of phenolic polycondensate resins from Egyptian bagasse pith were investigated previously [3, 5]. Optimum conditions for preparation of phenolic polycondensate resin from Egyptian eichhornia crassipes (EEC) were investigated by Sayyah *et al.* [6]. The introduction of such resin in the pores of the paper sheet by dipping technique to improve the insulating properties for different industrial purposes has not been investigated before.

The present work also deals with the investigation of the d.c electrical resistivity of such materials of cellulosic filter paper which has a crosslinked structure in the presence of resins which were impregnated through the filter paper. This can be used for various purposes such as electric shielding [7], prevention of static electricity accumulation [8], heating [9], *etc.*

Various authors [10 – 12] have studied the electrical properties of grafted carbon black for the purpose of developing a resistor device and a surface heater.

The Egyptian Eichhornia Crassipes (EEC) which hinders the navigation in the river Nile can then be exploited in a useful way. The EECP – phenol resin was once modified with phenol – formaldehyde and once modified with phenol – benzaldehyde, with different aldehyde concentrations. It is rather interesting to investigate the resistivity variations in relation to the temperature and the concentration of the three types of resins when impregnated through the cellulosic filter paper.

2. EXPERIMENTAL

2.1. Materials

The raw material used was Egyptian eichhornia crassipes (EEC) obtained from El-Gezira zone (on the river Nile) at Beni Suef, Egypt. The EEC was normally dried then screened using sieve with 40 mesh, to reject the fibers and filler bundles. Sufficient quantity of EECP was collected and well mixed together to impart homogeneity to the starting material for this study. The mean values from three analysis of the raw material are given in Table 1.

TABLE 1 Characterization of the raw material (EEC) powder

Reaction name	*Content* (*wt.* %)
Hot water solubility	2.05
1% sodium hydroxide solubility	15.60
Holocellulose	68.75
Resistant cellulose	42.30
Lignin	11.75
Pentosan	19.20
Ash	17.40

The solid dry content after normal dryness was 89.17%. All chemical reagents were of chemically pure grade.

2.2. Methods

2.2.1. Preparation of EEC–Phenol Resin

The reaction was carried out in a two-necked flask, equipped with a reflux condenser and a thermometer. The optimum conditions for preparation and purification of EEC–phenol polycondensate resins was previously studied by Sayyah *et al.* [6]. The weight ratio of EECP/phenol was 2 : 1 (referred to the dry content); the volume of conc. HCl (9.25 N) was 25 ml, *i.e.*, 0.231 mol/25 ml of acid; the reaction temperature was 95–100°C, the optimum reaction time was 3 hours. After introducing the calculated quantities of EECP, phenol and catalyst (conc. HCl), the mixture of the reactants was well mixed and refluxed for 3 hours. At the end of the reaction, the product was cooled, filtered and neutralized with 0.1 N ammonium hydroxide solution and washed with hot water, then steam distilled to remove the unreacted phenol, then filtered and finally dried. The dry product was dissolved in ethyl alcohol and filtered to remove the insoluble matter.

2.2.2. Resistivity Measurements

The d.c resistivity measurements for the prepared samples were carried out in the temperature range from room temperature up to 100°C. The two electrode technique was used in the resistivity measurements. A power supply type EJ 123 was used, the current was detected by a digital electrometer, type HP-425 A, and the temperature was detected by using a chromel–alumel thermocouple. The overall error in the resistivity measurements did not exceed ± 2%.

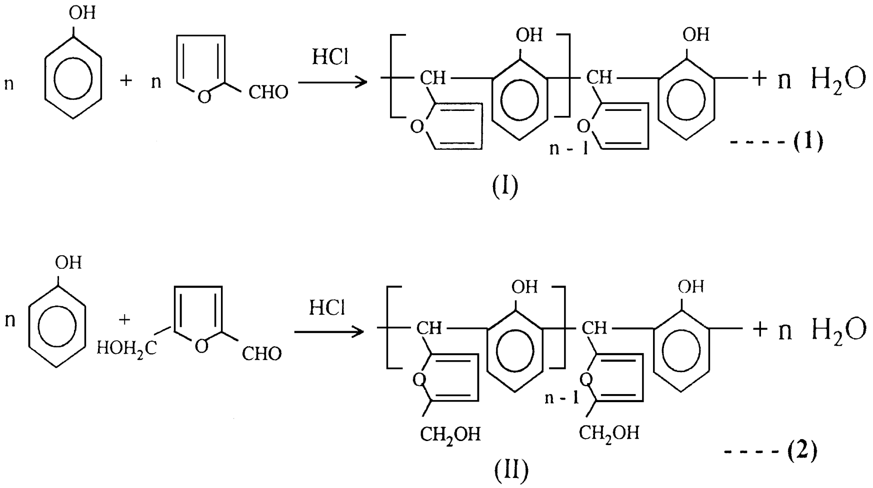
3. RESULTS AND DISCUSSION

3.1. Structure of the EECP–Phenol Polycondensate Resin

The element analysis of the produced resin is given in Table 2. The chemical formula is in good agreement with the found data. The pattern of the chemical reaction depends upon the hydrolysate products which may be present during the condensation reaction. The main constituents of the EECP is holocellulose and lignin as shown in Table 1. Holocellulose gives in the acid hydrolysis furfural and hydroxymethyl furfural (HMF) [4]. Therefore the pattern of the chemical reaction is assumed to be as shown in Scheme 1. In presence of conc. HCl at 85°C lignin gives about 10 products which contain carbonyl groups [13]. The average calculated chemical

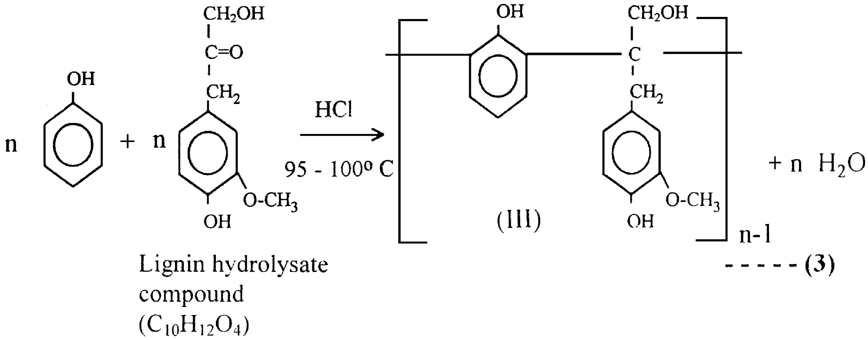
TABLE 2 Elemental analysis and the proposed structure of the resin

	C%		*H%*		*Molecular*	*Structure*
Resin name	*Calc.*	*Found*	*Calc.*	*Found*	*formula*	(*Schemes* 1, 3)
Phenol–Furfural	76.74	76.20	4.65	4.00	$C_{11}H_8O_2$	I
Phenol–Holocellulose	76.74	–	4.65	–	$C_{11}H_8O_2$	I
	71.29	–	4.95	–	$C_{12}H_{10}O_3$	II
	Average calculated data for I and II and the found data					
	74.02	74.80	4.80	5.10		
Phenol–Lignin	70.59	–	5.88	–	$C_{16}H_{16}O_4$	III
	73.89	–	6.40	–	$C_{25}H_{26}O_5$	IV
	Average calculated data for III and IV and the found data					
	72.24	73.85	6.14	6.90		
Phenol–EECP	76.74	–	4.65	–	$C_{11}H_8O_2$	I
	71.29	–	4.95	–	$C_{12}H_{10}O_3$	II
	70.59	–	5.88	–	$C_{16}H_{16}O_4$	III
	73.89	–	6.40	–	$C_{25}H_{26}O_5$	IV
	Average calculated data for I, II, III and IV and the found data					
	73.13	72.90	5.47	5.80		



SCHEME 1

formula of these hydrolysate compounds is $C_{10}H_{12}O_4$. On the other hand, the condensation of lignin model compounds with phenol under acid catalysis was investigated by Kratzl *et al.* [14], which gave the chemical reaction between phenol and lignin as shown in Eq. (4). All reactions of lignin model and lignin hydrolysate with phenol are represented in Scheme 2. The magnitude of degree of polymerization "*n*" depends upon the reaction conditions. Resins with higher viscosity values are known to possess larger values of "*n*" [15].



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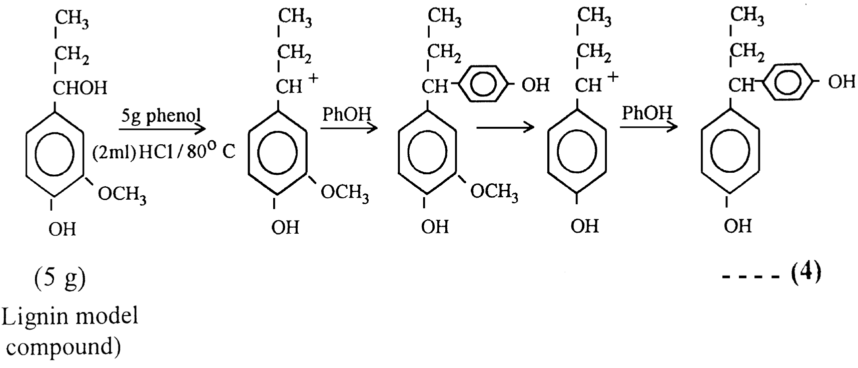
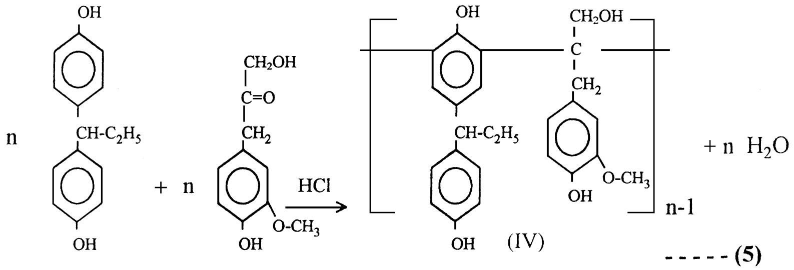


---- (4)

The compound produced from Eq. (4) can react with the compound produced from the acid hydrolysis of lignin ($C_{10}H_{12}O_4$) as follows.



----- (5)

SCHEME 2

3.2. Modification of EEC–Phenol Resin

The aim of these experiments was to see whether high yield and better insulating properties can be obtained by further condensing the EEC–phenol resin produced at the optimum condition [6] with phenol and formaldehyde or phenol and benzaldehyde.

The reaction was carried out in a three-necked flask equipped with stirrer, a reflux condenser and a thermometer. Equal amount of EEC–phenol polycondensate resin and freshly distilled phenol (10 g for each) were charged. Half of the calculated quantity of formaline solution 37% or benzaldehyde and sulfuric acid (1 ml) were introduced. The reaction was carried out in glacial acetic acid as a medium (30 ml) at 70°C with stirring for one hour. After cooling down to room temperature, the second half of the aldehyde and sulfuric acid were then added, stirring with water till neutral, mixed with ethyl alcohol (5 ml) and steam distilled till free from phenol. After drying the product to constant weight, the yield, specific viscosity and drop falling temperature were determined. It was found that the highest yield of the soluble resin (88.9%) was obtained by the addition of 2.6 g formaldehyde and (50.5%) by the addition of 5 g benzaldehyde. The data are summarized in Tables 3 and 4.

The structures of the two modified resins are represented in Scheme 3.

3.3. Infrared Spectroscopic Studies

The infrared spectra of the pure dry resins are represented in Figure 1. The following characteristic bands appear in the infrared spectra:

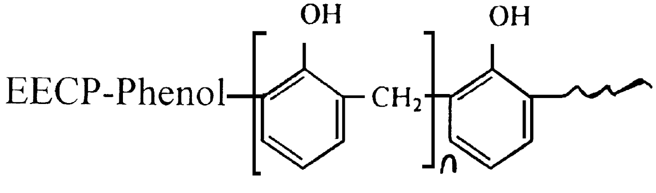
(a) The broad band at 3262 cm^{-1} in case of EECP-phenol resin, and the broad band at 3361 cm^{-1} in case of the modified resin with phenol formaldehyde or phenol–benzaldehyde are attributed to strong and medium hydrogen bonded OH group, respectively.

TABLE 3 Effect of formaldehyde quantity in grams upon the yield, specific viscosity, and drop-falling temperature of the produced linear resin

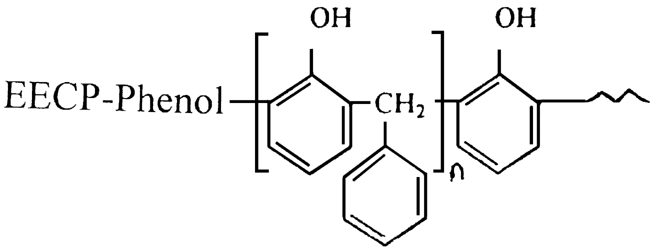
No.	*Formaldehyde quantity (g)*	*Yield (%)*		*Specific viscosity (η_{sp})*	*Drop falling temperature DFT (°C)*
		Linear	*Cross linked*		
1	1.1	63.30	0.00	0.070	65
2	1.5	66.05	0.00	0.085	70
3	1.9	78.54	6.85	0.113	85
4	2.6	88.49	11.95	0.145	130
5	3.4	42.74	57.69	0.090	85

TABLE 4 Effect of benzaldehyde quantity in grams upon the yield %, specific viscosity, and drop-falling temperature of the produced linear resin

	Benzaldehyde	*Yield* (%)		*Specific viscosity*	*Drop falling temperature*
No.	*quantity* (*g*)	*Linear*	*Cross linked*	(η_{sp})	*DFT* (°*C*)
1	2.52	29.95	23.42	0.029	115
2	3.32	43.15	10.47	0.044	120
3	5.00	50.50	11.19	0.059	130
4	10.00	43.82	16.35	0.044	105
5	20.00	14.08	47.68	0.029	100



Modified resin with phenol and formaldehyde



Modified resin with phenol and benzaldehyde

SCHEME 3

(b) A weak band at 3087, 3170 and 3127 cm^{-1} for CH symmetric stretching vibrations in benzene ring in case of EECP – phenol, modified resin with phenol formaldehyde and phenol benzaldehyde, respectively.

(c) A weak band at 2978, 2936 and 2957 cm^{-1} for CH symmetric stretching vibration of CH_3 group in case of the three types of resins 1, 2 and 3 respectively.

(d) The medium bands at 1703 and 1766 cm^{-1} are attributed to a weak overtone and combination band for CH in benzene ring and for C=C stretching vibration in furan ring in case of EECP – phenol and the two modified resins, respectively.

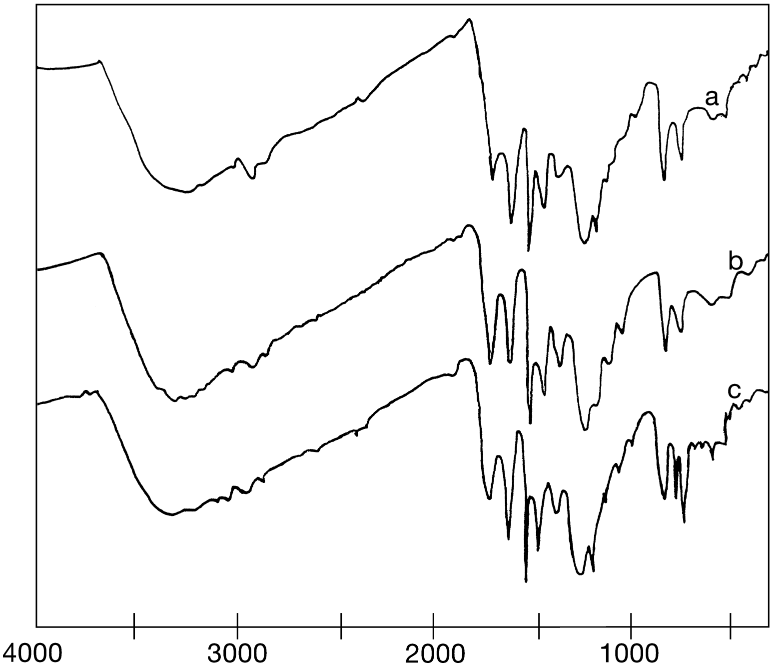


FIGURE 1 Infrared spectra of the prepared resins. (a) EECP–phenol resin, (b) EECP–phenol modified with phenol and formaldehyde, and (c) EECP–phenol modified with phenol and benzaldehyde.

(e) A sharp band in the region 1660–1608 cm^{-1} for C=C stretching vibration in benzene ring.

(f) A sharp band at 1511 cm^{-1} in case of resin (1) and two sharp bands (one split band) at 1489 and 1553 cm^{-1} in case of resin (2), at 1532 and 1574 cm^{-1} in case of resin (3).

(g) The sharp band at 1450, 1425 and 1426 cm^{-1} is attributed to δ(O—CH_3) and R—O—Ar ether or scissor vibration of CH_2 groups in case of the three investigated resins (1, 2 and 3) respectively.

(h) A sharp band in the region 1298–1261 cm^{-1} for CH_2 external deformation.

(i) A weak band at 1170 cm^{-1} for OH deformation vibration in phenolic systems.

(j) Two bands at 1042 and 1105 cm^{-1} are attributed to the OH deformation of primary alcohols, which assures the presence of aliphatic OH groups.

(k) A sharp band at 833 cm^{-1} is attributed to out of plane CH deformation, characteristic for 1,4 substitution in benzene ring and CH rocking vibrations. The band at 750 cm^{-1} is attributed to 1,2 substitution in benzene ring.

The infrared spectroscopic analysis confirms the proposed chemical formula in Table 2. The chemical structure of the produced resin is an alternation of furan units and lignin hydrolysate units in the resin chain. This is in good agreement with that found in case of bagasse pith-phenol polycondensate by Sayyah *et al.* [5].

3.4. Study of the Minimum Adsorbed Resin Weight Percentage on the Paper Sheet

Filter paper (Whatman No. 1) was used for the preparation of the impregnated sheets. The dimensions of the sheet were 1.5 cm width, 10 cm length and 0.16 mm thickness. The paper sheets were dipped in the different resins (1, 2 and 3) solutions in acetone for 30 seconds at 25°C. Different concentrations of each resin were prepared in order to study the effect of resin concentration on the adsorbed resin quantity on the paper sheet. The treated sheets were placed between two filter papers and passed 6 times through rollers of 5 kg weight to remove the excess solution. After drying in air, sheets were heat treated at 100°C for 30 minutes in as electric oven. The data are graphically represented in Figure 2, from which we find that the maximum adsorbed resin weight percentage on the paper sheet reaches at the 2% resin concentration.

3.5. Electrical Properties

The electrical resistivity (ϱ) of such materials depends on the presence of charge carriers not connected chemically with the macromolecules. The resistivity (ϱ) of these materials is high due to the low mobility of charges. It is known that conduction results from the transport of carriers, of either sign, from one position to another which requires an activation energy. Usually ϱ is described by the following relation

$$\varrho = \frac{1}{nq\mu} \tag{6}$$

where n is the number density of charge carriers, q is the charge, of either sign, and μ is the mobility of charges.

The ϱ values for all samples in the whole range of temperature varied from 10^5 to $10^9\,\Omega\cdot\text{cm}$. A look at these values may give the impression that conduction has a semiconducting nature, but the log ϱ versus T relations do not indicate such behavior. This is why the study of the electrical conduction mechanism in such materials is so interesting.

In order to solve this ambiguity, a study of the chemical structure of such materials should be useful. The filter paper is a cellulosic crosslinked structure which has the formula ($C_6H_{10}O_3$) n where n is the number of repeat units, see Scheme 4. From the structure it is clear that it is rich in oxygen, especially that which acts as ether linkages. Such linkage has two pairs of

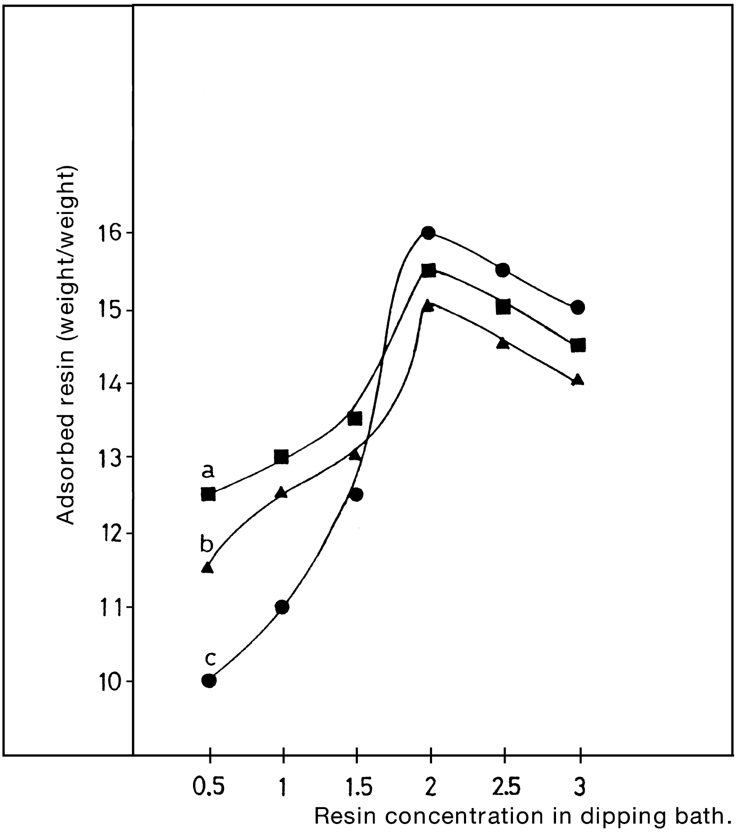
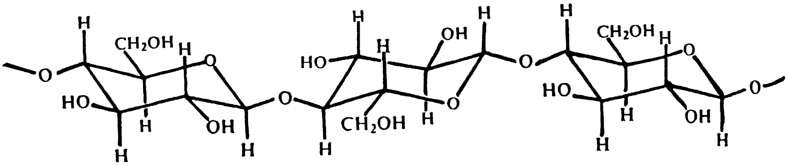


FIGURE 2 Relation between resin concentration in dipping bath and absorbed resin on paper sheet. (a) resin modified by phenol and formaldehyde, (b) resin, and (c) resin modified by phenol and benzaldehyde.



SCHEME 4

unbonded electrons which are responsible for electrical conduction. The existence of free electrons in a crosslinked structure together with the large distance between oxygen atoms could be the reason of the generally high resistivity. Moreover, the oxygen atoms are separated by carbon atoms which form a σ-band, which could also contribute to the high ϱ values of the filter paper.

The presence of resin molecules in the pores of the filter paper blocks the vacancies in it. The conduction in the resin itself is ionic due to the ionization of phenolic OH groups [16]. When the electrons travel from one oxygen site to another, some of the free electrons are captured by the positively charged hydrogen ions in the OH groups. This could lead to an increase in the resistivity.

The way to interpret our results is through the parameters n and μ included in Eq. (6), either solely or dually, in terms of the structural constituents of the samples over the whole range of temperature. Since μ in these materials is very low in the presence of applied low electric fields, a considerable increase in the ϱ-values means that the number density of charges in Eq. (6) can be the main origin of such increase.

Referring back to the structure, Figure 2 indicates that the percentage adsorption impregnated into the filter paper has a maximum for all samples when the resin concentration is 2%. Figures 3–5 show the log $\varrho - T$ relations at resin concentrations (c), 0.5% and 2%, together with the filter paper without resin impregnation as a reference for comparison. These figures yield a maximum value of ϱ for each sample when $c = 2\%$.

Figure 6 shows the log $\varrho - T$ relations for the three types of resin having $c = 2\%$ together with the non-impregnated filter paper. From this figure, the ϱ values were found to be the lowest for the non-impregnated filter paper. One may also notice that the EECP–phenol resin when modified with phenol formaldehyde gives ϱ values higher than those when the same resin is modified with phenol benzaldehyde. In the case of resin EECP–phenol modified with phenol formaldehyde, the methylene group acts as a conjugate aliphatic aldehyde residue unit, causing an increase in the resistivity of the resin. While in the case of resin EECP–phenol modified with phenol benzaldehyde, the presence of a phenyl ring which is attached to the methine group in the residual benzaldehyde moiety with an electron resonance and hence delocalization takes place. Such delocalization contributes to the decrease in the resistivity.

It is known that the three types of resin have branched structures, and the resin here acts as a filler filling the void spaces within and between the structure constituents of the filter paper sheet. Electrical conduction occurs along molecules contacting each other or separated by small gaps. These interaggregate gaps may be considered as potential barriers for charges to hop by tunneling. Reduction of the gap affects the flow of charges. The average interaggregate distance is affected by many parameters including structure, concentration, size and shape of the aggregates, size distribution, mixing efficiency, temperature, *etc.* [17].

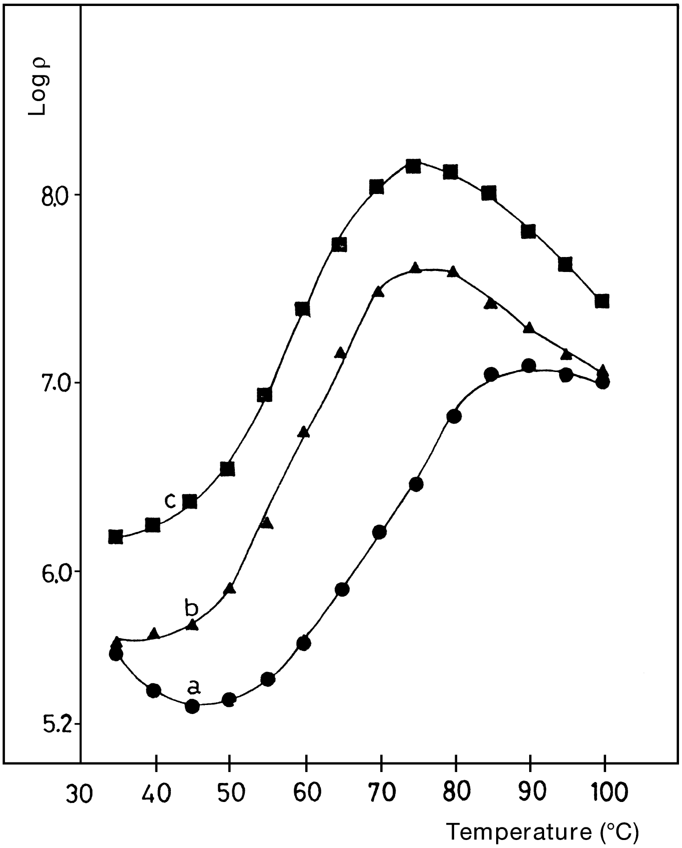


FIGURE 3 Relation between log ϱ and temperature for EECP–phenol resin using different concentrations. (a) paper without impregnation, (b) impregnated paper ($c = 0.5\%$), and (c) impregnated paper ($c = 2\%$).

Conductor-insulator composites become resistive only after a certain threshold concentration of the resistive filler has been added [17]. The critical percolation threshold represents a system where continuous chains have been first formed. The resistive elements of these chains are either making contacts between themselves or separated by very small distances across which the charges can hop by tunneling.

The resin molecules have been chosen as the intercalant because their molecular radius is small, and hence they can be easily arranged between the layers without destroying the structure. The introduction of resin molecules into the van der Waals slots of the original structure, the filter paper, starts in the close-to-contact region, leading to an even increase in its resistance

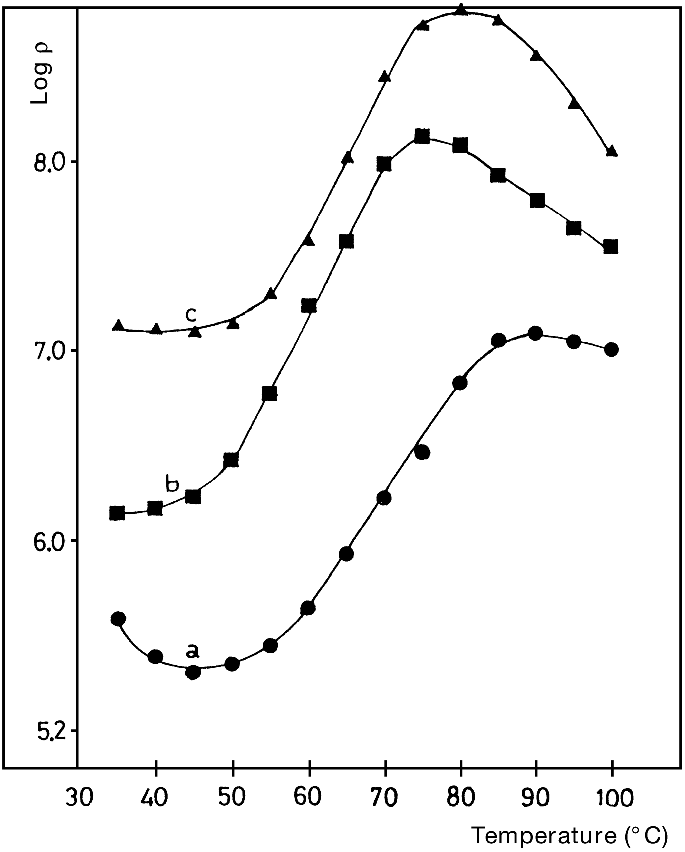


FIGURE 4 Relation between log ϱ and temperature for resin modified with phenol–formaldehyde using different concentrations. (a) paper without impregnation, (b) impregnated paper ($c = 0.5\%$), and (c) impregnated paper ($c = 2\%$).

and respectively to a decrease in the van der Waals forces between the neighboring layers [18]. This in turn leads to the increase in the resistivity of our samples as observed in our measurements.

Referring to Figure 6, we see that at low temperatures (below 50°C) the resin fills the void spaces within and between molecules and the gaps separating them become very small. Reduction of space gaps which are considered as potential barriers for charge carriers affects their mobility (μ). This effect has a little significance at low T and therefore the decrease of ϱ with the increase in T during this range is mainly due to the increase in the number of charge carriers.

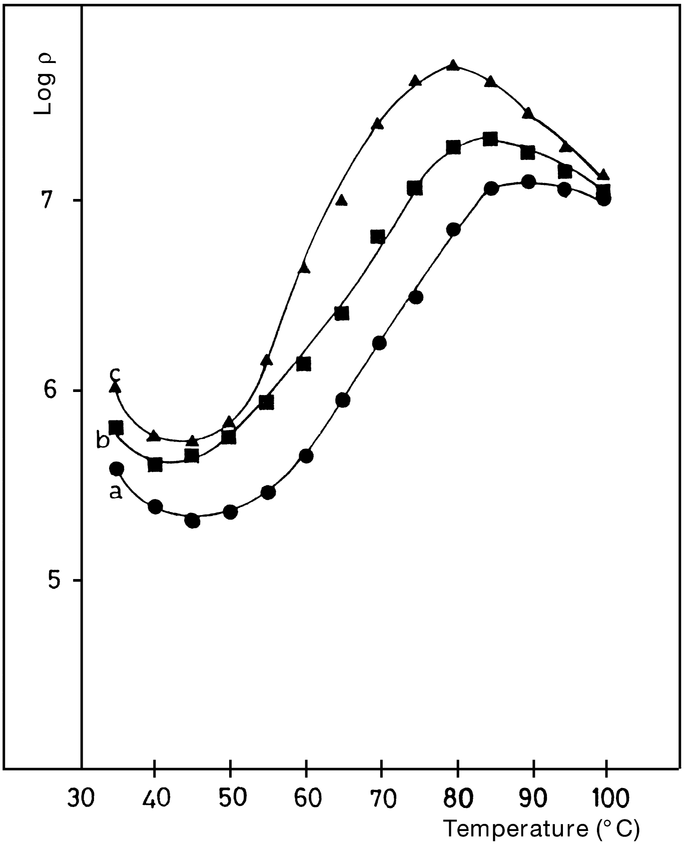


FIGURE 5 Relation between log ϱ and temperature for resin modified with phenol–benzaldehyde using different concentrations. (a) paper without impregnation, (b) impregnated paper ($c = 0.5\%$), and (c) impregnated paper ($c = 2\%$).

At medium temperatures (from 50°C to 80°C), and as T increases through this range of T, the space gaps get bigger and therefore thermal activation energy needed for charge carriers to hop becomes higher. Therefore, the number of carriers (n) which could acquire this high energy decreases. As a result, ϱ starts to increase because the small contribution of the mobility of charges (μ) to the resistivity. The relation between ϱ and T showed a metal-like behavior until it reaches its maximum value for all types of resin.

At high temperatures (above 80°C), expansion of the resin within the sample occurs as T increases in this range. Consequently, the activation energy required for hopping becomes larger and hence decreases the number of charge carriers which contributes to conduction, even though the

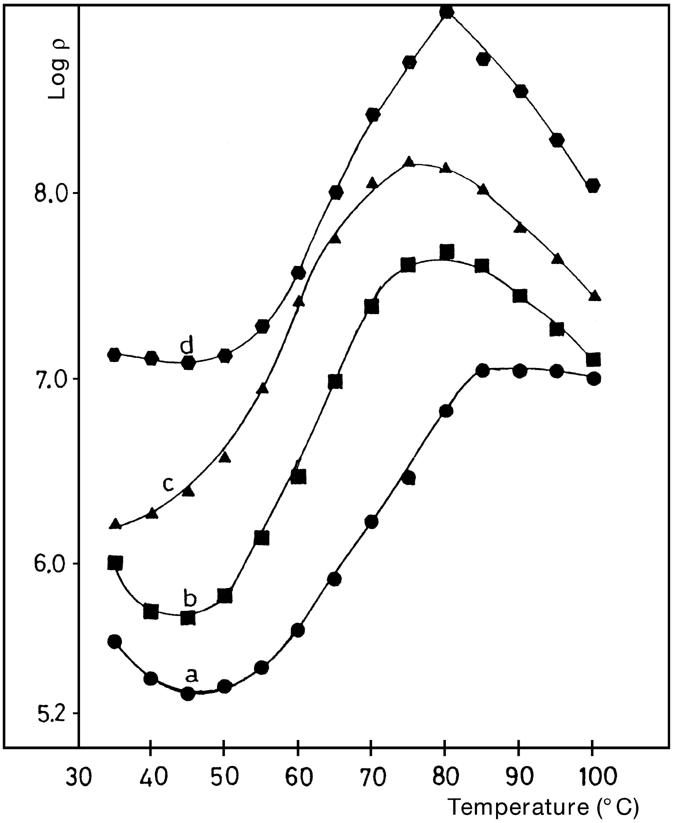


FIGURE 6 Relation between log ϱ and temperature for the three types of resin using the 2% concentration. (a) paper without impregnation, (b) resin modified by phenol–benzaldehyde, (c) EECP–phenol resin, and (d) resin modified by phenol–formaldehyde.

mobility (μ) increases with T. Therefore, in this temperature range the product $n \cdot \mu$ in Eq. (1) gives rise to a decrease in the resistivity.

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