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Development of glass-like carbon from phenol formaldehyde resins employing monohydric and dihydric phenols

R. K. AGGARWAL, G. BHATIA, O. P. BAHL, M. MALIK*
Carbon Technology Unit, Division of Materials, National Physical Laboratory, Dr K. S. Krishnan Road, New Delhi 110 012, India

A study on the development of glass-like carbon from phenol formaldehyde resins employing monohydric (simple) and dihydric phenols (resorcinol and catechol) has been made. It is revealed that to obtain a good glass-like carbon, the optimum molar ratio of formaldehyde to resorcinol in the resorcinol formaldehyde resin is 1.5, as was found earlier in the case of a simple phenol formaldehyde resin, whereas for catechol formaldehyde resin, the optimum molar ratio of formaldehyde to catechol is found to be 2.0. Further, it is observed that the three types of resins lead to glass-like carbons of essentially the similar characteristics, except that the catechol formaldehyde based carbons possess the highest strength of 326 MPa. A mechanism has been proposed on the basis of three types of phenolic rings designated as attached, bridging and cross-linking, in the structure of the three cured phenol formaldehyde resins to explain the respective optimum molar ratio of formaldehyde to type of phenol.

1. Introduction

Glass-like carbon is a new carbon material which combines some of the properties of glass, namely, lustre, imperviousness and mode of fracture, with the other physical and chemical properties of carbon. It is being produced in various shapes and sizes from a variety of thermosetting resins under different trade names by various manufacturers. Most of the scientific investigations concerning this carbon relate to its properties and applications [1–9], whereas only a few relate to its method of preparation [10–14]. In view of this, work was initiated in this direction. The present authors have already reported [15, 16] the studies on the synthesis of phenol formaldehyde (PF) resins having different molar proportions of phenol (P) and formaldehyde (F) as well as on the subsequent carbonization of these resins to glass-like carbon. The aim therein was to optimize the formaldehyde to phenol (F/P) molar ratio in the PF resin for its use as a precursor in the development of glass-like carbon. The methodology used in the studies was the hot moulding of the resin into plates of size 60 mm × 20 mm × 4 mm. The optimum F/P molar ratio was found to lie between 1.45 and 1.60, and the characteristics of glass-like carbons obtained from such a resin were seen to compare well with those of the best commercially available ones.

The above optimization work was extended to other phenol formaldehyde resin systems by replacing the simple phenol with dihydric phenols, namely, resorcinol and catechol. These two dihydric phenols have the same molecular formula but differ in the relative positions of the two hydroxyl groups attached to the parent benzene ring. Preliminary work on the use of these dihydric phenols revealed the inapplicability of the previous hot moulding technique to resorcinol and catechol formaldehyde resin systems, because of the quicker setting nature of these resins compared to the simple phenol formaldehyde resin. However, the technique of liquid casting and curing proved to be a satisfactory means of shaping these resins. Further, for the sake of a good comparison, the development of glass-like carbon from simple phenol formaldehyde resin having an already optimised F/P molar ratio of 1.5 was also carried out using the present liquid casting technique.

Some results of the development of glass-like carbons from resorcinol formaldehyde resin have already been reported by the present authors [17]. However, the present paper gives a detailed account of the results obtained in the case of all three phenols (two dihydric and one monohydric) and also the possible mechanism in each case which explains the optimum molar ratio of the formaldehyde to type of phenol obtained in the respective cases. The optimization was made with respect to a number of characteristics of the glass-like carbons resulting from the three phenol formaldehyde resin systems.

2. Experimental details

In the case of simple phenol formaldehyde resin, a single batch of the resin was synthesized from simple phenol and formaldehyde taken in a previously optimized F/P molar ratio of 1.5 [16]. In the cases of resorcinol (R) and catechol (C), however, a series of resins of each type were made by varying the formal-

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*Present address: National Thermal Power Corporation, Singrauli, Uttar Pradesh, India.

TABLE I Characteristics of glass-like carbons made from phenol formaldehyde resin (F/P = 1.5) using casting and hot moulding techniques

Characteristics	Casting technique	Hot moulding technique*
Green density ($\mathrm{g\,cm^{-3}}$)	1.25	1.24
Baked density ($\mathrm{g\,cm^{-3}}$)	1.53	1.50
Carbonization yield (%)	65.4	68.4
Volume shrinkage (%)	45.5	44.2
Linear shrinkage (%)	18.0	17.0
Open porosity (%)	0	1.0
Transverse breaking strength (MPa)	274	138
Electrical resistivity ($\mathrm{m\Omega\,cm}$)	14.1	7.9

*Data taken from the earlier work [16].

dehyde to dihydric phenol molar ratio (F/R or F/C) in the range 1.15 to 4.0. In general, the reactants were mixed together and heated carefully in the presence, or absence, of a catalyst (ammonia) under reflux conditions at a temperature of 50 to 90° C until the resins were formed. In particular, no catalyst was required in the case of resorcinol formaldehyde resin, whereas ammonia, 2% by weight of the simple phenol or catechol, was found necessary for the formation of simple phenol and catechol formaldehyde resins. The various batches of resins were then densified at a temperature of 50 to 70° C in the presence or absence (for resorcinol) of para-toluene sulphonic acid (PTSA), taken 2% by weight of the resin, under partial vacuum varying around 40 cm of mercury till a suitable consistency (honey-like) was obtained. Then from each batch, ten glass tubes of 20 cm length and 4 mm diameter were filled. These resin-filled tubes were heated at a temperature of 70° C for about 24 h, when the resin solidified. The resin rods so formed were taken out of the glass tubes. These rods were cured at 200° C for 1 h and subjected to the green density measurement. These were then packed in a graphite boat with a high-purity natural graphite powder and carbonized to a temperature of 950° C in an atmosphere of UHP-grade nitrogen. The glass-like carbon rods, so obtained, were characterized with respect to various properties, namely, carbonization yield, bulk density, kerosene density, volume shrinkage, linear shrinkage, open porosity, transverse breaking strength, electrical resistivity and scanning elecron microscopy as per their usual methods described elsewhere [15].

The variations of these characteristics obtained in the case of the three resin systems are given in Tables I to III and an inter-system comparison is given in Table IV.

3. Results and discussion

3.1. Glass-like carbons from simple phenol formaldehyde resin system

Table I shows the characteristics of the glass-like carbons (rods) made from the simple formaldehyde resin by the casting technique, having a F/P molar ratio of 1.5, along with those of the similar carbons (plates) made using the previous hot moulding technique [16]. It is seen here that most of the characteristics of the carbons made by the two techniques are essentially the same, except the transverse breaking strength which in case of the casting technique is found to be double that of those made by the other technique. This observation can be attributed mainly to two reasons, (1) the open porosity which is zero in the former case compared to 1% in the latter and (2) the size effect according to which the higher the dimensions of the specimen, the lower will be its strength. The area of cross-section in the former case is much lower compared to that in the latter case. The observations on open porosity are confirmed from the morphological studies of the fractured surface of the present glass-like carbons (rods) as well as the previous ones (plates), obtained using a scanning electron microscope. The micrographs so obtained are shown in Figs 1a and b which indicate a smooth glass-like surface in the former case and a fine porosity in the submicron range in the latter case. Further, the scanning electron micrograph of the commercial glass-like carbon also reveals a fine porosity in the submicron range, as shown in Fig. 1c which is similar to that observed in the case of hot-moulded glass-like carbon.

3.2. Glass-like carbons from resorcinol formaldehyde resin

Table II summarizes the characteristics of glass-like carbons made from several resorcinol formaldehyde resins having F/R molar ratio varying from 1.15 to 3.0. It is seen that, in general, the green density of the glass-like carbons decreases with increase in the F/R molar ratio. The bulk density, however, is found to be almost the same, i.e., lying in the range 1.48 to 1.50 $\mathrm{g\,cm^{-3}}$ in all the cases except the one with F/R equal to 1.15. This may be attributed mainly to an

TABLE II Characteristics of glass-like carbons made from resorcinol formaldehyde resins having different formaldehyde-to-resorcinol molar ratios

Characteristic	Formaldehyde to resorcinol molar ratio					
	1.15	1.3	1.5	2.0	2.5	3.0
Green density ($\mathrm{g\,cm^{-3}}$)	1.42	1.39	1.31	1.21	1.26	1.28
Bulk density ($\mathrm{g\,cm^{-3}}$)	1.45	1.49	1.50	1.49	1.48	1.48
Kerosene density ($\mathrm{g\,cm^{-3}}$)	1.45	1.44	1.45	1.46	1.46	1.47
Carbonization yield (%)	63.0	60.4	61.2	59.7	60.3	59.4
Volume shrinkage (%)	38.4	43.6	46.5	51.5	48.6	48.3
Linear shrinkage (%)	14.8	16.7	18.5	21.1	19.9	20.0
Open porosity (%)	0	0	0	0	0	0
Transverse breaking strength (MPa)	232	232	256	247	252	266
Young's modulus (GPa)	25.4	28.4	25.4	25.7	29.4	30.6
Electrical resistivity ($\mathrm{m\Omega\,cm}$)	11.4	11.0	10.9	10.6	10.6	10.3

TABLE III Characteristics of glass-like carbons made from catechol formaldehyde resins having different formaldehyde to catechol molar ratios

Characteristics	Formaldehyde to catechol molar ratio					
	1.3	1.5	2.0	2.5	3.5	4.0
Green density ($g\,cm^{-3}$)	1.43	1.44	1.41	1.36	1.38	1.38
Bulk density ($g\,cm^{-3}$)	1.53	1.54	1.53	1.52	1.53	1.53
Carbonization yield (%)	66.5	66.7	65.3	65.0	64.2	63.9
Volume shrinkage (%)	37.5	37.9	39.4	41.8	42.1	42.5
Linear shrinkage (%)	14.5	14.9	15.6	16.4	16.7	16.9
Transverse breaking strength (MPa)	238	300	326	286	277	270
Electrical resistivity ($m\Omega\,cm$)	10.5	11.1	11.2	10.4	11.1	10.4

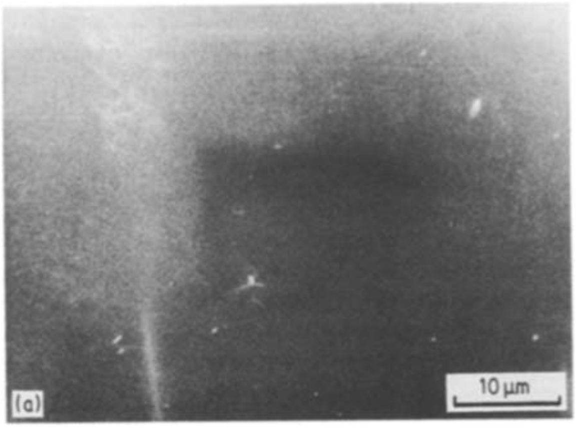
TABLE IV A comparative data of the characteristics of glass-like carbons made from different phenol formaldehyde resins

Characteristics	Glass-like carbons made from			
	Simple phenol formaldehyde resin		Resorcinol formaldehyde resin	Catechol formaldehyde resin
Green density ($g\,cm^{-3}$)	1.25	(1.24)*	1.31	1.41
Baked density ($g\,cm^{-3}$)	1.53	(1.50)	1.50	1.53
Carbonization yield (%)	65.4	(68.4)	61.2	65.3
Volume shrinkage (%)	45.5	(44.2)	46.5	39.4
Linear shrinkage (%)	18.0	(17.0)	18.5	15.6
Transverse breaking strength (MPa)	274	(138)	256	326
Open porosity (%)	0	(1.0)	0	0
Electrical resistivity ($m\Omega\,cm$)	11.1	(7.9)	10.9	11.2

*Figures in the parentheses refer to the characteristics of glass-like carbons made by the hot moulding technique.

increasing volume shrinkage observed with increase in F/R molar ratio. Further, within the experimental error, the kerosene density of glass-like carbons in all the cases was found to be the same as their bulk density implying thereby that the open porosity in these carbons is nearly zero.

The transverse breaking strength is more or less the same (247 to 266 MPa) in all the cases except the ones with F/R molar ratios of 1.15 and 1.30. Lastly, the electrical resistivity is found to vary between 10.3 to 11.4 mΩ cm. It may be noted here that the characteristics of glass-like carbons and their precursor resins are essentially the same in cases with F/R varying between 1.5 and 3.0. Therefore, from the techno-economic point of view, the resorcinol formaldehyde resin with a F/R molar ratio of 1.5 is the most suitable one [17]. The scanning electron micrograph of the glass-like carbon made from such a resin is shown in Fig. 2 which reveals an impervious structure similar to that of glass.



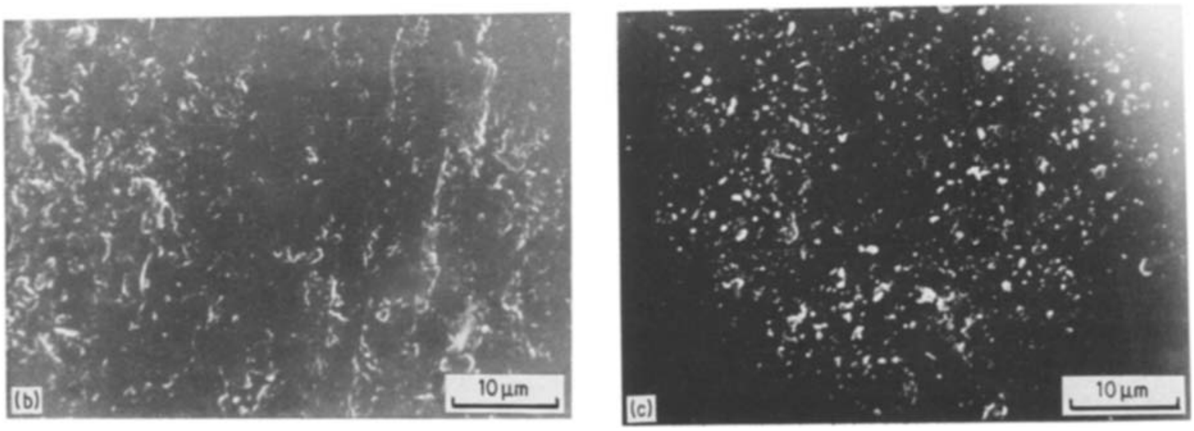


Figure 1 Scanning electron micrograph of glass-like carbon made from phenol formaldehyde resin using (a) casting technique and (b) hot moulding technique. (c) Scanning electron micrograph of commercial glass-like carbon.

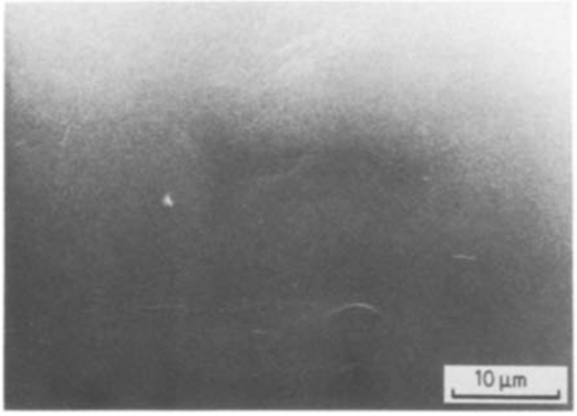


Figure 2 Scanning electron micrograph of glass-like carbon made from resorcinol formaldehyde resin (F/R molar ratio of 1.5) using casting technique.

3.3. Glass-like carbons from catechol formaldehyde resin

Table III gives a summary of the characteristics of glass-like carbons (rods) made from several catechol formaldehyde resins having F/C molar ratio varying in the range 1.3 to 4.0. It is evident that the green density, in general, decreases with the increase in F/C molar ratio, whereas the baked density is found to be almost the same in all cases. These observations can be attributed mainly to increasing volume and linear shrinkages with increase in the F/C molar ratio. Further, the transverse breaking strength is found to increase from 238 to 326 MPa as the F/C molar ratio increases from 1.3 to 2.0, beyond which it decreases gradually.

The kerosene density of the glass-line carbons at F/C molar ratio of 2.0 is found to be the same as their bulk density. This implies that the open porosity in these carbons is almost zero like that observed in the case of resorcinol formaldehyde resin based glass-like carbons. This observation agrees with the scanning electron micrographs of the glass-like carbons shown in Figs 3a and b. It can be seen from the micrographs (Fig. 3a) that in carbons based on F/C molar ratio of 2.0, there are no pores. However, in carbons based on F/C molar ratio of 1.5, pores with a size of 1 to 2 μm are observed (Fig. 3b). Lastly, the electrical resistivity does not show a significant pattern of variation with the F/C molar ratio.

From the above discussion, it could be concluded that the optimum F/C molar ratio for the development of glass-like carbon from catechol fromaldehyde resin is 2.0.

3.4. A comparison of characteristics of glass-like carbons from different phenol formaldehyde resins

The characteristics of glass-like carbons made from the three phenol formaldehyde resins have been compared and summarized in Table IV. It is clear from this table that simple phenol formaldehyde resin leads to glass-like carbons (casted rods and moulded plates) possessing the characteristics of a good glass-like carbon. However, the transverse breaking strength of the glass-like carbons made from this resin using the casting technique is double that of the carbons made using the hot moulding technique. This has been attributed to the size effect and to nearly zero porosity in the former case. Further, a comparison of the characteristics of glass-like carbons made from the three phenol formaldehyde resin systems by the casting technique shows that all of these resins lead to glass-like carbons having essentially the same properties as those of the good commercially available glass-like carbons. However, the catechol formaldehyde resin leads to carbons which possess the highest strength among the three resin systems.

4. Proposed mechanism

4.1. Simple phenol formaldehyde resin system

The first step in the reaction of phenol and formaldehyde is the formation of addition compounds known as methylol derivatives, in which the addition takes place at the ortho and para positions of the phenolic ring. These products which may be considered for subsequent polymerization, are formed most satisfactorily under neutral or alkaline conditions. However, in the presence of alkaline catalyst and with more of formaldehyde (resole-grade resin), the methylol phenols can condense either through methylene linkages or through ether linkages [18, 19]. In the latter case, subsequent loss of formaldehyde may occur with

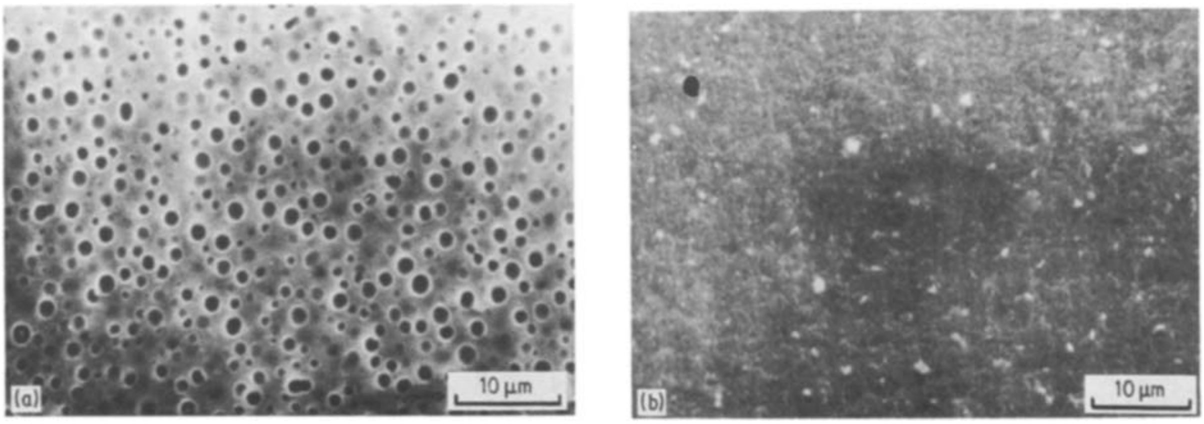


Figure 3 Scanning electron micrographs of glass-like carbons made from catechol formaldehyde resin, based on F/C molar ratio of (a) 1.5 and (b) 2.0.

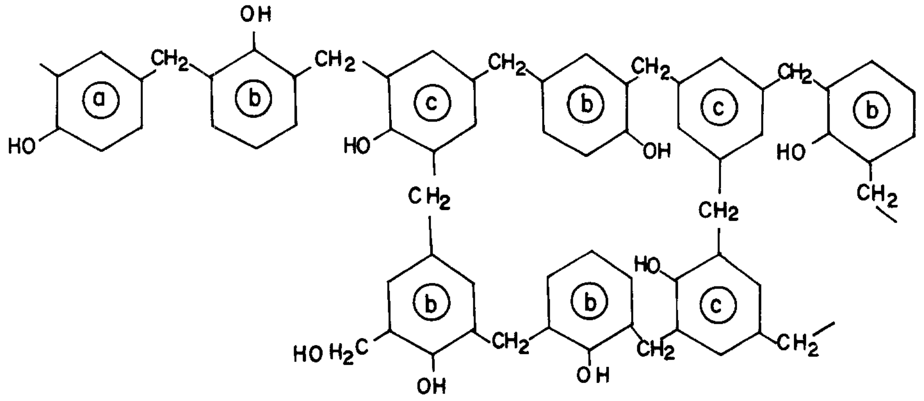


Figure 4 Structure of cured phenol formaldehyde resin.

methylene bridge formation. If the reaction is carried further, a large number of phenolic nuclei can condense to give a network formation as shown in Fig. 4 wherein the following three types of phenolic rings may be distinguished [20]:

(i) Attached rings (those carrying only one methylene bridge) which may also carry none, one or two free methylol groups at the ortho and para positions leading to three possibilities in all, as shown in Fig. 5a, corresponding respectively to F/P ratios of 0.5, 1.5 and 2.5 giving rise to an average F/P value of 1.5.

(ii) Bridging rings (those carrying two methylene bridges) which may also carry none or one free methylol group as shown in Fig. 5b, leading to two possibilities which correspond to F/P values of 1.0 and 2.0 respectively, with an average F/P value of 1.5.

(iii) Cross-linking rings (those carrying three methylene bridges) which cannot carry any free methylol group leading to only one variety as shown in Fig. 5c with a F/P value of 1.5.

It is therefore clear that whatever may be the configuration of phenolic rings in the structure of cured phenol formaldehyde resin, the most probable F/P molar ratio comes out to be 1.5, which lies in the range of F/P 1.45 to 1.60 found experimentally for the phenol formaldehyde resin leading to the best properties of the resulting glass-like carbons.

4.2. Resorcinol formaldehyde resin system

The reasons for the completion of reactions between formaldehyde and resorcinol at a molar requirement of 1.5 and subsequent conversion to glass-like carbon of comparatively superior properties could be seen from the mechanism which is similar to that described above for simple phenol formaldehyde resin.

The presence of two hydroxyl groups in case of resorcinol results in an increased probability of reactions taking place at 2, 4 and 6 positions of the phenolic ring compared to the probability of such reactions in the case of simple phenol. This can be easily seen from structures I and II.

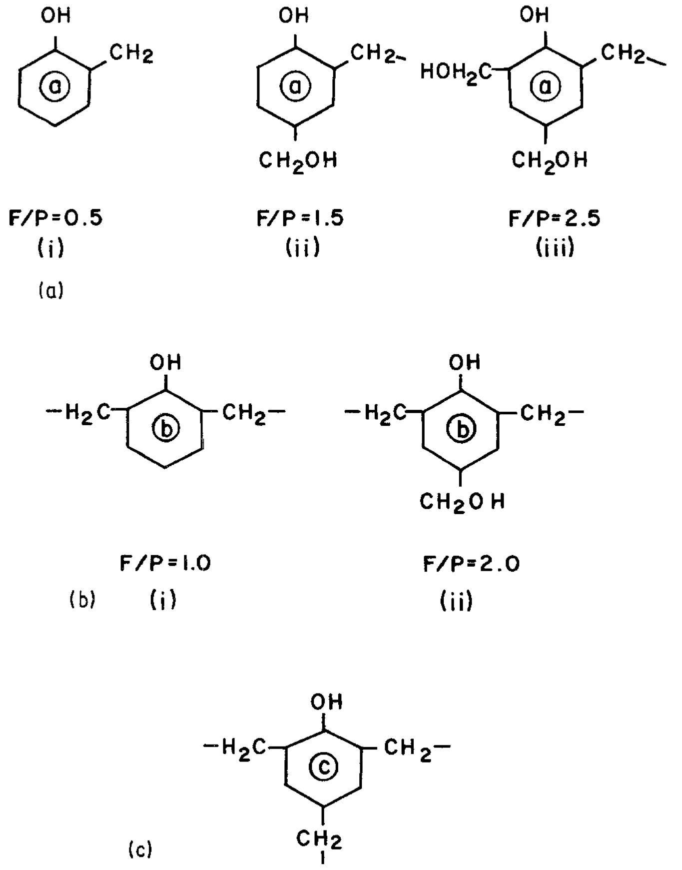
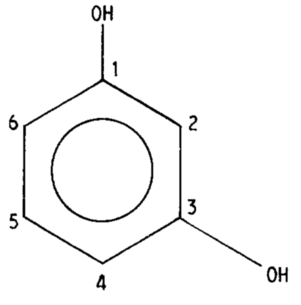
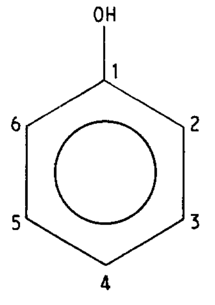


Figure 5 Three types of phenolic rings in the structure of cured simple phenol formaldehyde resin. (a) Attached rings carrying (i) no free methylol group (ii) one free methylol group and (iii) two free methylol groups. (b) Bridging rings carrying (i) no free methylol group and (ii) one free methylol group. (c) Cross-linking rings carrying no free methylol group.



(I) Resorcinol



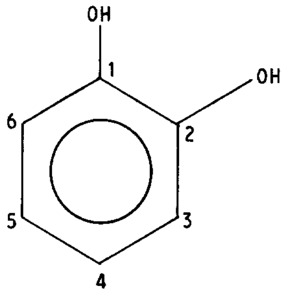
(II) Phenol

However, the mechanism of substitution reactions taking place in resorcinol and in the resorcinol formaldehyde resin are similar to those for the simple phenol or the phenol formaldehyde resin indicating again the presence of three types of phenolic rings, namely, attached, bridging and cross-linking, in the structure of cured resorcinol formaldehyde resin as shown in Fig. 6, each type having an average F/R molar ratio requirement of 1.5, thus giving rise to an overall F/R molar ratio requirement also of 1.5, which has been experimentally found to be the optimum giving rise to glass-like carbons of superior characteristics.

4.3. Catechol formaldehyde resin system

The mechanism in the present case is similar to the one applied for the simple phenol formaldehyde and resorcinol formaldehyde resins which indicates that F/C ratio of 2.0 is optimum for getting a good catechol formaldehyde resin capable of giving glass-like carbons of superior properties.

In the case of catechol, the presence of two hydroxyl groups at positions 1 and 2 as shown in structure III results in an increased number of sites i.e. four, for the substitution reactions to take place (positions 3, 4, 5 and 6 of the phenolic ring) compared to three sites each in case of simple phenol and resorcinol. The structure of cured catechol formaldehyde resin proposed is given in Fig. 7. It is seen again that three types of phenolic rings can be distinguished which are as follows:



(III) Catechol

(i) Attached rings which may carry none, one, two or three free methylol groups at the three vacant sites. This leads to four possibilities as shown in Fig. 8a possessing respectively F/C molar ratios of 0.5, 1.5, 2.5 and 3.5. This gives rise to a statistical average value of F/C as 2.0.

(ii) Bridging rings which may carry none, one or two free methylol groups as shown in Fig. 8b leading to three possibilities requiring F/C molar ratios of 1.0, 2.0 and 3.0, respectively, with a statistical average F/C value of 2.0.

(iii) Cross-linking rings which may carry none or one free methylol group leading to only two varieties as shown in Fig. 8c requiring F/C molar ratios of 1.5 and 2.5, respectively, with a statistical average F/C value of 2.0.

Therefore, it is quite clear that in all configurations of the phenolic rings in the structure of cured catechol formaldehyde resin, the most probable F/C molar ratio value works out to be 2.0. This value has been experimentally found to be optimum giving rise to glass-like carbons having the best properties.

5. Conclusions

1. The characteristics of glass-like carbons made from the simple phenol formaldehyde resin by the two techniques of casting and hot-moulding are found to be similar except the transverse breaking strength and open porosity, which in former case are 274 MPa and 0% compared to 138 MPa and 1% respectively in the latter case.

2. The optimum formaldehyde-to-type of phenol molar ratios (F/R or F/C) in the case of resorcinol and catechol formaldehyde resins, for the development of glass-like carbon, have been observed to be 1.5 and 2.0 respectively.

3. A comparison of the three phenol formaldehyde resins shows that all of them lead to glass-like carbons with essentially the same characteristics, with the exception that catechol based glass-like carbons possess the highest strength (326 MPa).

4. Theoretical mechanisms based on three types of

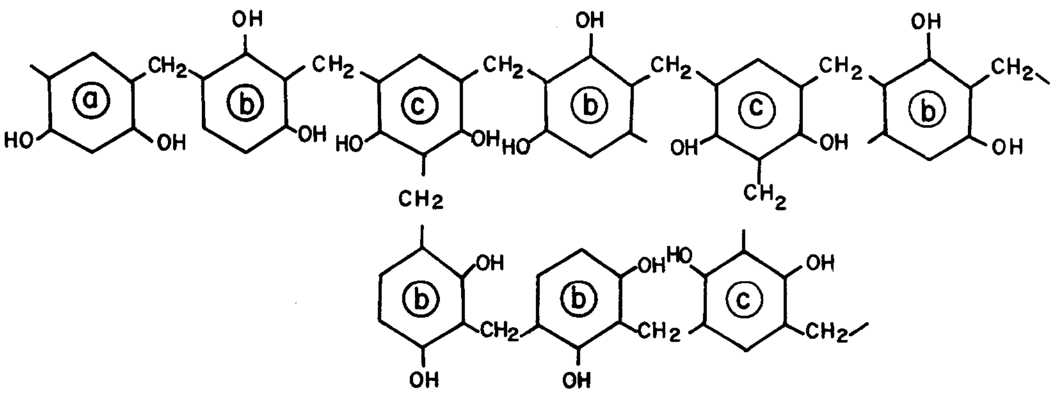


Figure 6 Structure of cured resorcinol formaldehyde resin.

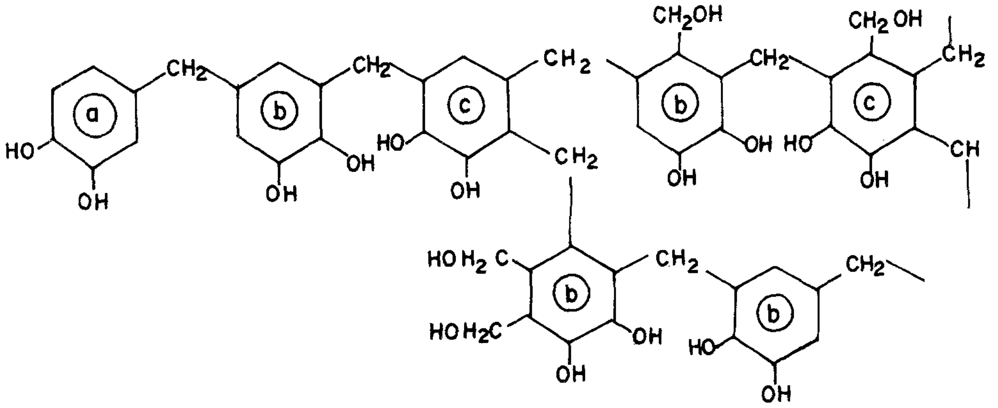


Figure 7 Structure of cured catechol formaldehyde resin.

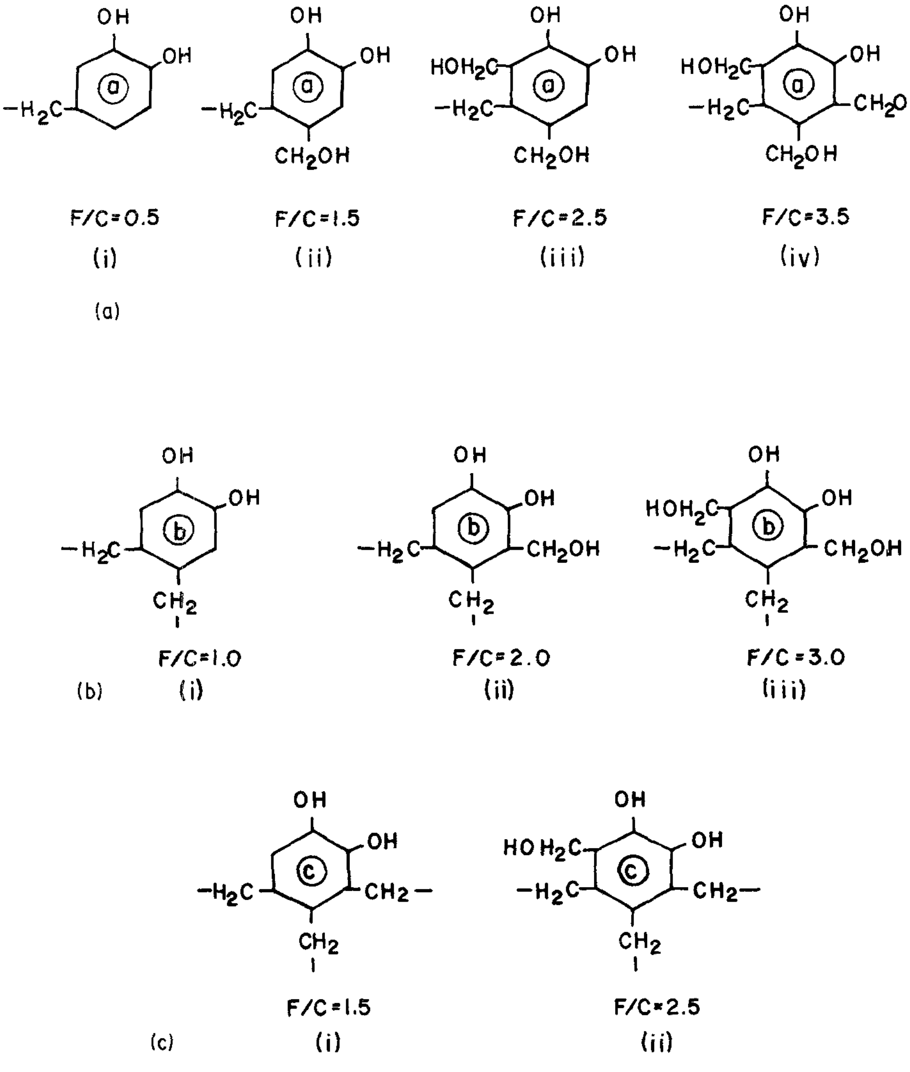


Figure 8 Three types of phenolic rings in the structure of cured catechol formaldehyde resin. (a) Attached rings carrying (i) no free methylol group, (ii) one free methylol group, (iii) two free methylol groups, and (iv) three free methylol groups. (b) Bridging rings carrying (i) no free methylol group, (ii) one free methylol group and (iii) two free methylol groups. (c) Cross-linking rings carrying (i) no free methylol group, and (ii) one free methylol group.

phenolic rings, namely, attached, bridging and cross-linking, in the structure of the cured resins, have been proposed to explain the optimum molar ratio of formaldehyde to type of phenol, obtained in the three phenol formaldehyde resin systems which result in glass-like carbons having best properties in the respective cases.

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