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Conversion of phenol formaldehyde resin to glass-like carbon

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Glass-like carbons have been produced for many years by the careful carbonization of a variety of starting materials such as cellulose, phenol formaldehyde, polyfurfuryl alcohol, acetone furfuryldehyde and other suitable thermosetting resins. A number of publications have appeared in the literature concerning their characteristics and applications. However, little is known about the preparation procedure and its influence on the development of this form of carbon. The present paper incorporates the studies on the carbonization behaviour of a suitable phenol formaldehyde resin and on the optimization of the phenol to formaldehyde molar ratio in the resin, carried out with respect to the various physical characteristics of the resins and the resulting carbons. The implications of these studies have been disucussed in detail.

1. Introduction

Glass-like carbon is a relatively newer form of carbon which is attracting considerable interest in a number of industries. It came into existence in 1962 when it was first developed by Yamada and Sato [1]. A similar carbon was reported at nearly the same time by Davidson [2]. Since then, numerous publications have appeared in the literature concerning this carbon. Yamada *et al.* [3] and Lewis and co-workers [4, 5] have described the properties and applications of this form of carbon without regard to its method of production. Cellulose [2, 6], phenol formaldehyde [7–11], polyfurfuryl alcohol [12], acetone furfural [13], aromatic resins [14], and other polymers have been cited as precursory materials for this carbon. Fitzer and his co-workers [15–17] have presented an exhaustive account of the chemistry of formation and the properties of glass-like carbons made from polyfurfuryl alcohol, phenol formaldehyde resins and mixtures thereof, and have noticed that all of these lead to glass-like carbons with essentially the same physical properties. Good reviews on this carbon have been published by Yamada [18], McKee [19] and recently by Jenkins and co-workers [20, 21]. However, it may be noted that so far little systematic work has been reported on the preparation technique and its influence on the ultimate characteristics of this carbon. In view of this, it was proposed to carry out studies on the carbonization behaviour of a suitably prepared phenol formaldehyde resin, and on the optimization of the formaldehyde-to-phenol molar ratio in the phenol formaldehyde resin. In each case the evaluation of the product was done with respect to a number of physical properties.

2. Experimental details

For the study on the carbonization behaviour of phenol formaldehyde resin, a suitable quantity of phenol was reacted with formaldehyde (taken in a molar ratio of 1:1.3) in the presence of ammonia (4% by weight of phenol) as catalyst. The mixture was boiled under reflux conditions and the resin so obtained was densified under partial vacuum at a temperautre of 70° C in the presence of p-toluene sulphonic acid (2% by weight of the resin). It was then shaped into plates measuring 60 mm x 20 mm x 3 mm, which were cured in an oven at 200° C for 1 h and finally carbonized in an electrically heated furnace to temperatures of 350 to1250° C, in steps of 150° C, to obtain different batches. All these plates were then characterized with respect to various physical

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properties, namely, carbonization yield, bulk density, kerosene density, volume shrinkage, linear shrinkage, open porosity, pore size distribution, transverse breaking strength, shore hardness and electrical resistivity as per their usual procedures described elsewhere [22].

For the study on the optimization of the formaldehyde-to-phenol ratio in the phenol formaldehyde resin, various resins were made using ammonia catalyst (2% by weight of phenol) by varying the formaldehyde-to-phenol molar ratio from 1 to 3 by employing the same procedure as has been described above. The resins were shaped into plates which were cured at 200° C and then carbonized to a temperature of 950° C. Finally the carbonized plates were characterized with respect to the aforementioned set of properties. The variations of these characteristics obtained in the two studies have been plotted in Figs. 1 to 8.

3. Results and discussion

Fig. 1 shows the variations of yield, volume shrinkage and linear shrinkage of phenol formaldehyde resin based plates with increase in the temperature of heat treatment. It is observed that the yield falls sharply in the initial stage up to a temperature of about 650° C which corresponds to the evolution of major pyrolysis products, namely, H_2O, CH_4, CO and H_2 besides other low molecular weight components [16, 17]. Above 650° C, however, the rate of fall in the yield decreases gradually. Further, it is observed that the volume and linear shrinkages resulting from the condensation and crosslinking reactions taking place between the various molecular spieces follow an inverse pattern to that of the yield. It may be noted here that the volume shrinkage is around 2.5 times that of the linear shrinkage which is what is expected mathematically.

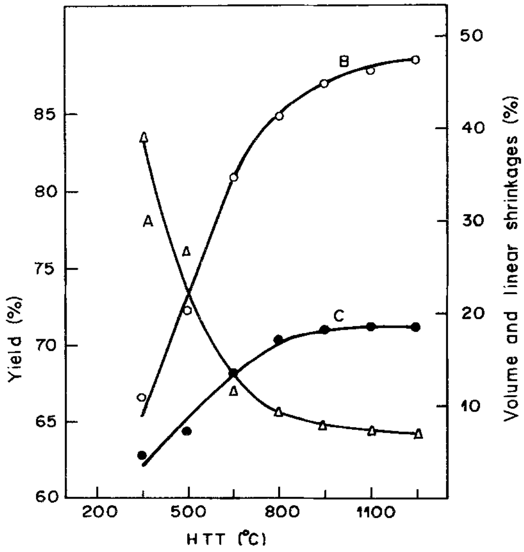

Figure 1 Variation of yield (A), volume shrinkage (B) and linear shrinkage (C), of phenol formaldehyde resin based plates with increasing temperature of heat-treatment.

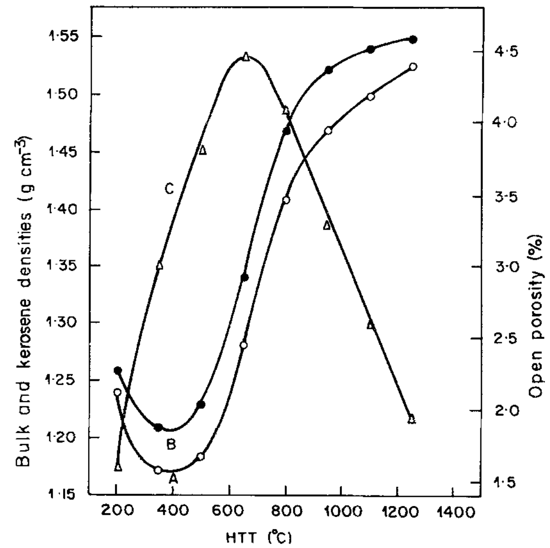

Figure 2 Variation of bulk density (A), kerosene density (B), and open porosity (C), of phenol formaldehyde resin based plates with increasing temperature of heat-treatment.

Fig. 2 represents the variations of bulk density, kerosene density and open porosity with the heat-treatment temperature. It is found that the bulk density first decreases with the heat-treatment temperature and attains a minimum value at 400° C, above which it starts increasing and continues to increase up to the highest temperature of 1250° C. The decrease in the bulk density in the temperature region of 200 to 600° C (compared to the bulk density at 200° C) may be due to the dominance of weight loss over the shrinkage, and the opposite effect could explain the increase in the bulk density in the heat treatment region above 600° C. Further, it is found that the kerosene density is always higher than the bulk density and follows a similar pattern to the bulk density as one would expect. Furthermore, the open porosity gradually increases with the heat-treatment temperature and attains a maximum value of 650° C beyond which it decreases gradually. The increase in the open porosity in the region 200 to 650° C corresponds

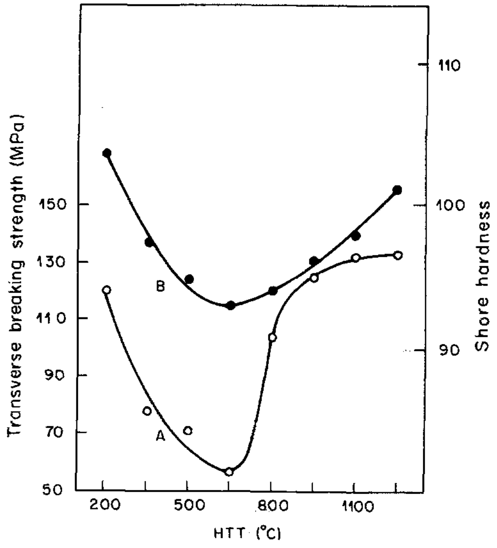

Figure 3 Variation of transverse breaking strength (A), and shore hardness (B), of phenol formaldehyde resin based plates with increasing heat-treatment temperature.

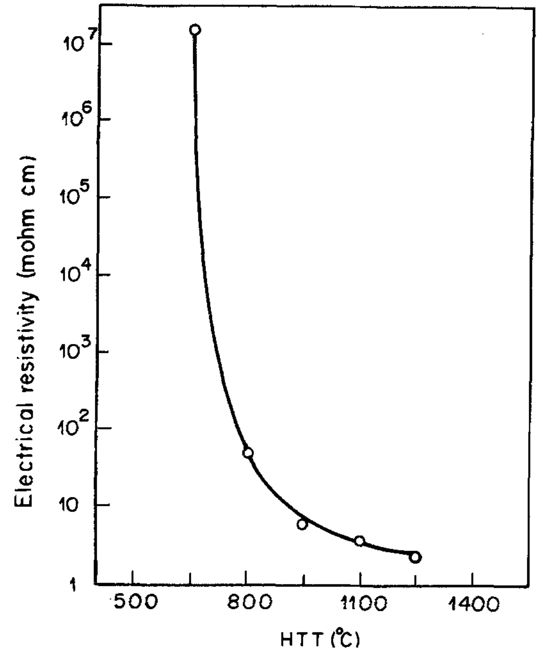

Figure 4 Variation of electrical resistivity of phenol formaldehyde resin based plates with increasing heat-treatment temperature.

to the increasing evolution of pyrolysis products, resulting in the creation and widening of pores. The decrease in the open porosity in the region 650 to 1250° C may be due to the narrowing and/or closing of the pores with a relatively decreasing amount of volatiles to escape.

Fig. 3 gives the variation of transverse breaking strength and shore hardness with the increase in the heat-treatment temperature. It is observed that the strength continuously decreases up to 650° C, above which it increases gradually. The decrease in strength appears to be related to the continuous increase in the open porosity. On the other hand, the increase in the strength above 650° C may be due to the gradual decrease in the open porosity and the size of pores. Further, the hardness of the plates is observed to vary essentially in a fashion similar to the transverse breaking strength.

Fig. 4 represents the electrical resistivity of the pyrolysed resin plates as a function of heat-treatment temperature. It is found that the resistivity falls sharply in the region of 600 to 800° C, beyond which the rate of fall in the electrical resistivity decreases gradually. This is true for the pyrolysis of all polymers.

Fig. 5 shows the variation in resin formation yield* with increase in the formaldehyde-to-phenol (F/P) molar ratio from 1 to 3. It is observed that the yield remains almost 100% up to a F/P ratio of 1.45, beyond which it decreases in a linear fashion. It is proposed that above a F/P ratio of 1.45, the excess amount of formaldehyde over that corresponding to the F/P value of 1.45 starts dissolving a part of the resin formed. Therefore, the decrease in the resin formation yield during which the F/P ratio increases from 1.45 to 3.0, could be due to an increasing amount of the resin getting dissolved in an increasingly excess quantity of formaldehyde. However, the dissolved part of the resin can be regenerated from the aqueous layer by boiling it with some added quantity of the catalyst.

Fig. 6 represents the variation of carbonization yield, volume shrinkage and linear shrinkage with increase in the F/P molar ratio. It is found that the yield increases sharply up to a F/P ratio equal to 1.3, remains almost constant in the F/P region 1.3 to 2.0, and finally decreases continuously with further increase in the F/P ratio. This could be explained as follows: in the first batch of resin having a F/P ratio of 1.0, the resin may have more low molecular components which come out during carbonization and thereby reduce the yield. The gradual increase in the carbonization yield

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*The resin formation yield was calculated with respect to the total weight of phenol and formaldehyde used.

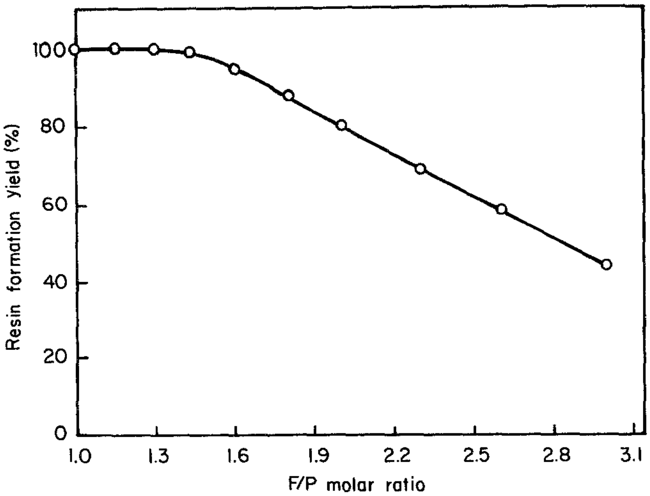

Figure 5 Variation of phenol formaldehyde resin formation yield with increasing formaldehyde-to-phenol (F/P) molar ratio.

may be attributed to the increasing amount of crosslinking of the resin molecules due to the increasing amount of methylene bridges, and also to the decreasing amount of low molecular weight species, both of which could result from the increasing amount of formaldehyde. The decrease in the yield beyond a F/P ratio of 2 could be due to the increasing number of free methylol groups attached to the various molecular species which are lost during the carbonization. The intermediate region of the F/P ratio 1.3 to 2.0 represents an optimum situation wherein there is minimum loss of weight due to low molecular weight components and free methylol groups.

As regards the volume and linear shrinkages, since these are associated with the evolution of pyrolysis products, they follow an inverse relation to yield.

Fig. 7 shows the curves of green density, bulk density, kerosene density, total porosity* and open porosity as a function of the F/P molar ratio. It is observed that the green density of the plates decreases only marginally over the entire range of formaldehyde variation. However, the bulk

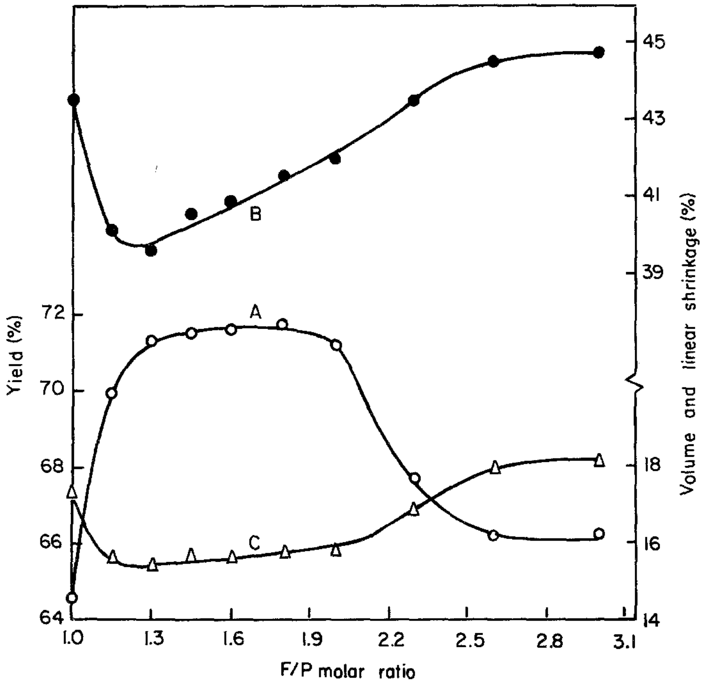

Figure 6 Variation of carbonization yield (A), volume shrinkage (B), and linear shrinkage (C), of various phenol formaldehyde resin based carbons with increasing F/P molar ratio.

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*The total porosity was calculated with respect to X-ray density of phenol formaldehyde resin based carbon taken as 2.127 g cm^{-3} at 950° C [23].

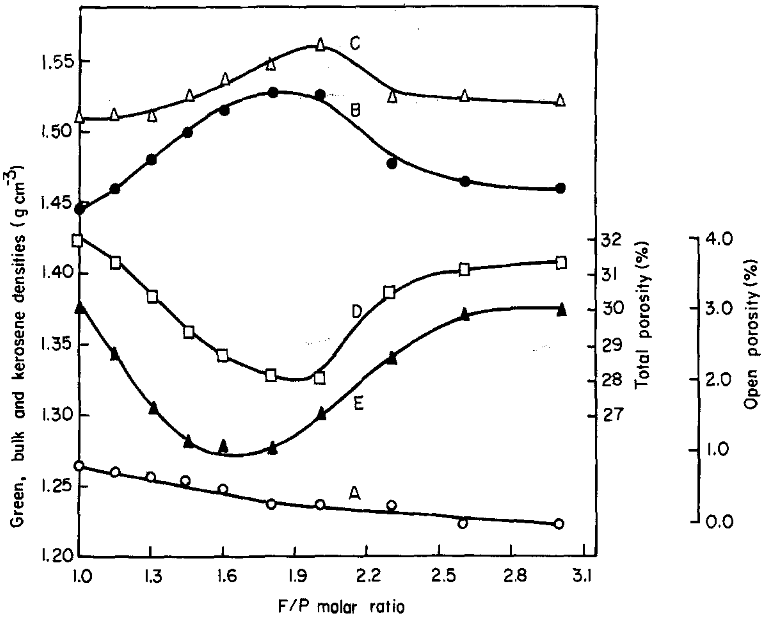

Figure 7 Variation of green density (A), bulk density (B), kerosene density (C), total porosity (D), and open porosity (E), of various phenol formaldehyde resin based carbons with increasing F/P molar ratio.

density gradually increases to a maximum and then decreases. This behaviour could be easily explained by considering the simultaneous variations of carbonization yield, volume shrinkage and green density. Further, the kerosene density is found to be always higher than the bulk density and vary in a fashion similar to that of the bulk density. Furthermore, the total porosity decreases gradually to a minimum at a F/P value of about 2.0, above which it increases. The decrease of total porosity during a F/P change from 1.0 to 1.3 could be due to the sharp increase in the carbonization yield against the relatively lower decrease in the volume shrinkage. Further decrease during the F/P change from 1.3 to 2.0 may be due to the gradual increase in the volume shrinkage with yield remaining essentially the same. Finally, the increase in the total porosity beyond the F/P value of 2.0 may be due to the dominating effect of decrease in the yield over that of the increase in volume shrinkage. As regards the open porosity, it is observed that it varies more or less in parallel with the total porosity. However, it may be noted here that the closed porosity (obtained from the difference in the ordinate values) increases gradually to a highest value at a F/P ratio of 1.45, above which it starts decreasing to attain a lowest value at F/P equal to 2.0. Above a F/P value of 2.0, however, there is a marginal increase in the closed porosity.

Fig. 8 represents the transverse breaking strength, shore hardness and electrical resistivity of various phenol formaldehyde resin based carbons with increasing F/P molar ratios. It is found that the transverse breaking strength increases sharply and attains a maximum value of more than 140 MPa at a value of F/P equal to 1.60. Beyond this F/P value, however, there is a sharp fall followed by a gradual one. The increase in the strength could be attributed to the decrease in the open and total porosities. The similar values of strength during the F/P region (1.45 to 1.80) could be mainly due to nearly the same values of open porosity in this region. Finally, the decrease in the strength above F/P equal to 1.80 may be because of the increase in the open and total porosities. Further, it is found that the shore hardness increases rapidly to a maximum value at a F/P ratio equal to 1.45, above which it decreases gradually up to a F/P value of 2.0 and remains almost the same in the subsequent region. Lastly, the electrical resitivity is observed to vary in a narrow range of 7.5 to 9.0 mΩ cm.

It is interesting to note here from Figs. 6 to 8 that phenol formaldehyde resins having a F/P molar ratio varying from 1.45 to 1.80 exhibit reasonably high values of bulk density, carbonization yield, transverse breaking strength and shore hardness along with reasonably low values of total and open porosity, However, the resin formation yield in the case of the resin with a F/P ratio of 1.80 is only 88% compared to 99 and 95%

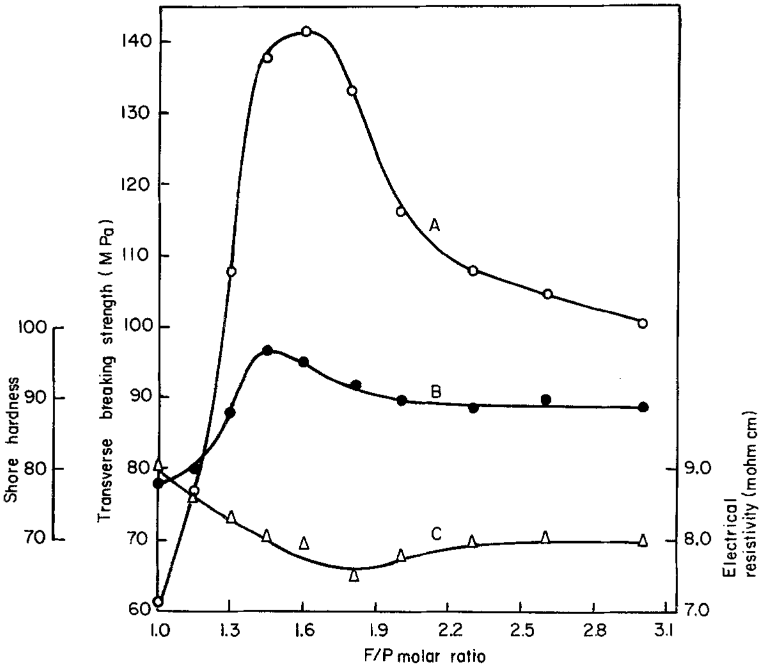

Figure 8 Variation of transverse breaking strength (A), shore hardness (B), and electrical resistivity (C), of various phenol formaldehyde resin based carbons with increasing F/P molar ratio.

in case of the resins with F/P equal to 1.45 and 1.60 respectively (Fig. 5). Therefore, considering the technical and economical aspects of the development of glass-like carbon, it could be said that the F/P molar ratio of 1.45 to 1.60 is the most suitable one. The characteristics of the glass-like carbon made using such a resin could be seen, from Table I, to compare well with those of the commercial glass-like carbon.

Further, it could be observed from Figs. 1, 2, 6 and 7 that a phenol formaldehyde resin with a F/P molar ratio of 1.30 and synthesized with 4% ammonia (by weight of phenol) has a carbonization yield of 64.6%, and leads to a glass-like carbon with an open porosity of 3.3%, whereas another resin with the same F/P ratio, but made using 2% ammonia, has a significantly higher carbonization yield (71.4%) besides resulting in a glass-like carbon having an open porosity of 1.6%. This suggests that 4% ammonia is more than the optimum amount of catalyst and causes the formation of a relatively greater amount of low

TABLE I Comparative data of the characteristics of NPL and commercial glass-like carbons

Characteristic number	Characteristic	NPL[a] glass-like carbon	Commercial[b] glass-like carbon
1	Bulk density (g cm^{-3})	1.50–1.52	1.50–1.55[c] 1.51[d]
2	Kerosene density (g cm^{-3})	1.52–1.54	1.54[d]
3	Total porosity (%)	28.7–29.4	29.3[d]
4	Open porosity (%)		Nil[c]
	(i) Kerosene	1.04–1.13	1.60
	(ii) Mercury[e]	0.20–0.46	0.57[d]
5	Transverse breaking strength (MPa)	138–142	100[c]
6	Young's Modulus (GPa)	29.0	27.9[c]
7	Shore hardness	95–97	120–125[c] 97–105[d]
8	Electrical resistivity (mΩ cm)	7.9–8.1	5.5[c]

[a] Refers to the formaldehyde-to-phenol molar ratio of 1.45 to 1.60; [b] refers to Le Carbone-Loraine, France V10 (HTT = 1000° C); [c] as per the manufacturer's claim; [d] as per the present authors' measurements; [e] using mercury porosimeter (pore size $\geqslant$ 7.5 nm).

molecular weight components that come out as volatiles during carbonization.

4. Conclusions

1. For the development of glass-like carbon from phenol formaldehyde resin, the formaldehyde-to-phenol molar ratio of 1.45 to 1.60 is the most suitable one from techno-economical considerations.

2. The 2% of ammonia catalyst (by weight of phenol) used in the synthesis of phenol formaldehyde resin leads to a significantly higher carbonization yield of the resin, and lower open porosity of the resulting glass-like carbon, as compared to the case of 4% ammonia catalyst.

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