PHENOL-FORMALDEYDE RESIN STRUCTURE FOR THE SYNTHESIS OF GLASSY CARBON

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INTRODUCTION

Phenol formaldehyde resins are used as precursors in the fabrication of glassy carbons [1]. Glassy carbons are hard, stiff (~25MPa), usually pore free structures with non wetting ultra smooth surfaces. Glassy carbons have been fabricated for the use in heart valve components as well as crucibles for glass melting. The ultimate performance and properties of these glassy carbons will be influenced by material processing which often involves the addition of water to reduce viscosity.

The developed glassy phase structure will be strongly dependent on the bonds formed during cure and on the initial microstucture of the cured phenol-formaldehyde (PF) resin. Phenol formaldeyde can polymerize into either the *novalac* (thermoplastic) or *resole* (thermoset) type structure or a combination of the two [2]. The resole and novalac structures are dependent on the ratio of formaldehyde to phenol (F:P). Excess formaldehyde will yield a resole type structure and excess phenol will yield the novalac type structure [3]. The F:P ratio will determine the concentration and nature of bonding, where the bond types will either be an ether link (-O-) or a methylene link (-CH_2-).

Figure 1 is a schematic of the condensation polymerization reactions for phenol-formaldehyde. The differences in bonding and structure (microtexture) produced during polymerization will yield distinct carbons as a function of heat treatment. Thermosets (resole) are hard carbons and therefore will not yield graphite even after experiencing temperatures in excess of 2000°C. This category of polymers produce glassy carbons. Thermoplastics (novalac) are soft carbons and will yield graphite (not glassy carbon) as a function of heat treatment.

The focus of the present work is to model the influence of water addition, cure temperature, and cure time on the structure and properties of phenol-formaldehyde resin as a precursor in the synthesis of glassy carbon.

EXPERIMENTAL METHOD

A phenol-formaldehyde resin known commercially as Varcum was used as the starting material. Water additions of 0, 10, and 20 wt% were made to the Varcum resin. Resin samples were all initially set-cured at 90°C. The cured resin samples were then heat treated at 146, 171, and 196°C for 4, 6, and 8 hour holds. Microhardness tests were conducted on all samples using a Shimadzu 2000 micro indentor.

A DSC analysis was used to determine T_g for each Varcum sample tested.

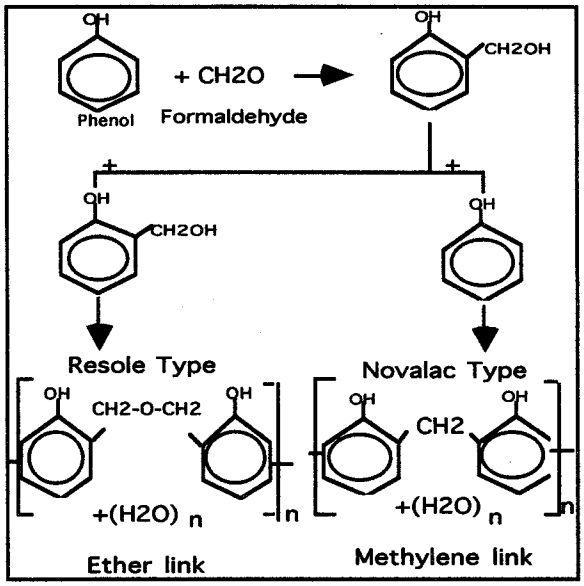

Figure1 Schematic illustrating the formation of the resole and novalac type structures.

RESULTS AND DISCUSSION

Figures 2 and 3 show plots of Vickers hardness versus cure temperature for Varcum samples with 0% and 20% water added and heat treated (cured) for 4, 6, and 8 hours.

Figures 4 and 5 show plots of Vickers hardness and T_g versus heat treatment time for two Varcum samples with 10% and 20% water added and heat treated (cured) at 146°C and 196°C .

These curves are an indication of bonding and micro-structural changes that are occurring within the resin as a function of water addition, heat treatment and heat treatment time. Water may provide a mechanism that would support novalac (-CH_2-) formation within an abundant resole structure. Figure 6 illustrates a model for the proposed structure observed in these resin systems.

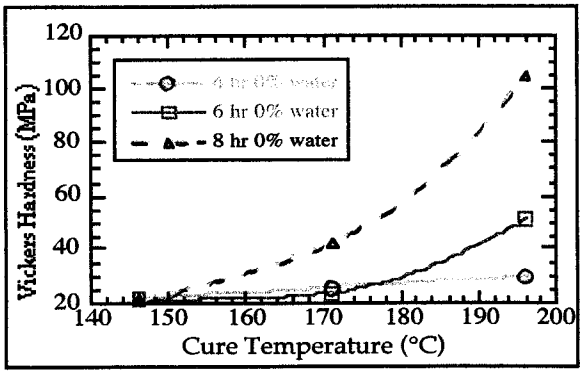

Figure 2 Vickers Hardness versus cure temperature for Varcum with 0% water added.

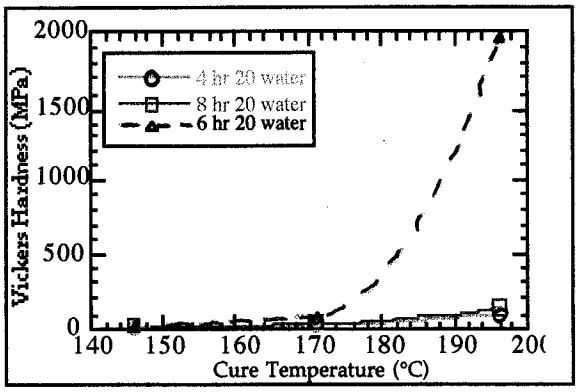

Figure 3 Vickers hardness versus cure temperature for Varcum with 20% water added.

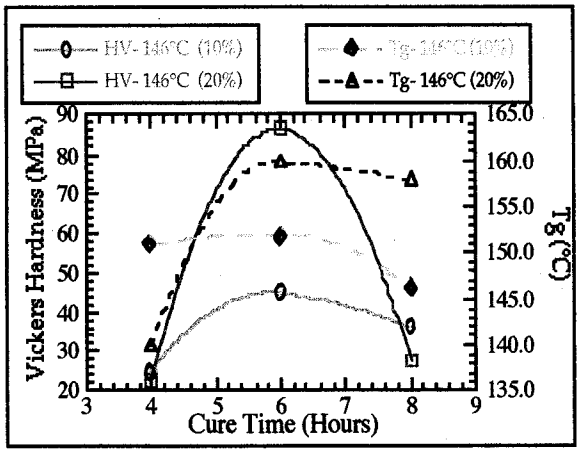

Figure 4 Vickers hardness and T_g versus time for two Varcum samples with 10% and 20% water added and heat treated at 146°C.

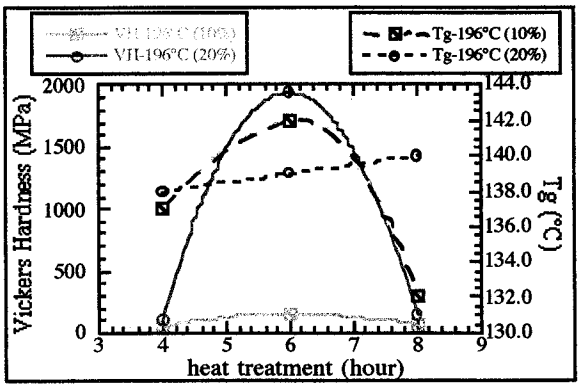

Figure 5 Vickers hardness and T_g versus time for two Varcum samples with 10% and 20% water added and heat treated at 196°C.

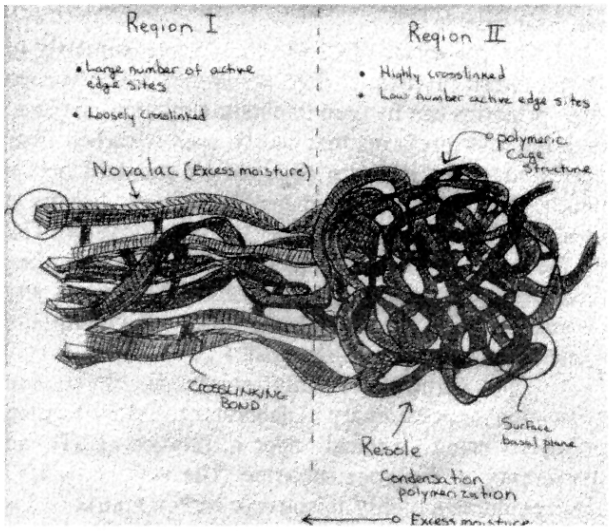

Figure 6 Model of proposed structure formed during cure and heat treatment of phenol-formaldehyde resin.

CONCLUSION

Broad distinctions in hardness and T_g are attributed to the influence of H_2O on bond formation. The role of H_2O in conjunction with cure time and heat treatment on the structure of glassy carbon continues to be a focus of this investigation.

REFERENCES

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2. Cambell, M. I., "Introduction to Synthetic Polymers", Oxford University Press 1994
3. Haupt, A., R., and Sellers T., Ind. Eng. Chem. Res **33**, 693 (1994)