STUDIES ON GLASS REINFORCED EPOXY RESIN USING VULKADUR-A AS CROSSLINKING AGENT BOTH IN PRESENCE AND ABSENCE OF CARBON BLACK AND OTHER NON-BLACK FILLERS

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Epoxy resin can be reinforced with glass (fabric form) in presence of Vulkadur-A, a phenol formaldehyde resin containing a hardening agent. Overall enhancement in mechanical properties has been found with stocks cured with Vulkadur-A containing 2·5 parts of carbon black as filler.

The choice of matrix resin in reinforced plastics is a matter of prime importance, since on it depend, many properties such as strength, ease of fabrication, resistance to service conditions (temperature, humidity etc.) and cost. Attempts have been made to utilise various types of resins to improve, particularly, the quality of the existing structural materials and to replace various other materials of general interest.

In this work, investigation on reinforcement of epoxy resin (Araldite CY & 230) with glass (fabric form) both in presence of carbon black and non-black materials as fillers and also in their absence has been carried out by measuring different mechanical properties of the composites. Infra-red spectra have been taken in case of unfilled stocks and a reaction scheme has been suggested to correlate the mechanical properties with the data obtained from spectral analysis.

MATERIALS AND METHODS

Araldite CY 230—It is an epoxide resin obtained from CIBA of India Ltd., Bombay.

Vulkadur-A—It is a Phenol Formaldehyde resin containing a hardening agent obtained from Bayer (India) Ltd., Bombay.

Carbon Black (SRF)—A product of Cabet, U.S.A.

Aluminium Oxide and Silica—These were of a chemically pure grade.

Glass Fabric—It was of a quality given in Table 1 and obtained from Fibre glass Pilkington Ltd., Bombay.

Lamination

Laminates were fabricated with heat cleaned woven glass fabric[1] and cured in a big david bridge curing press under heat and pressure. Mechanical properties of the composites namely tensile strength, hardness and bursting load were measured by known methods.[1]

Infrared Spectra

I.R. spectra* were taken with unfilled stock cured at 100° C for different cure times.

RESULTS AND DISCUSSION

The variation of tensile strength, Brinell hardness and bursting load with cure time at different temperatures is given in Fig. 1-3. The maximum values of tensile strength and bursting load at 180°C and 100°C

TABLE 1

QUALITY OF GLASS FABRIC

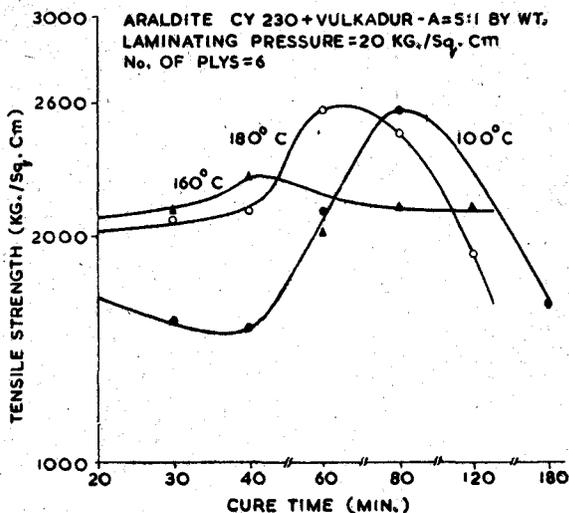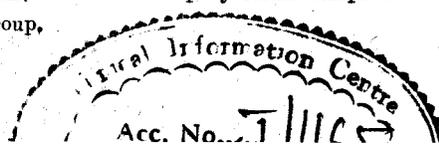| Type of glass	Warp	Weft	Wt/Sq. Yd.	Design
E	*Threads per inch*		4 ozs. (Appx.)	Plain weave
	60	44		

FIG 1—Variation of tensile strength with cure time at various cure temperatures for glass fabric epoxy resins composites.

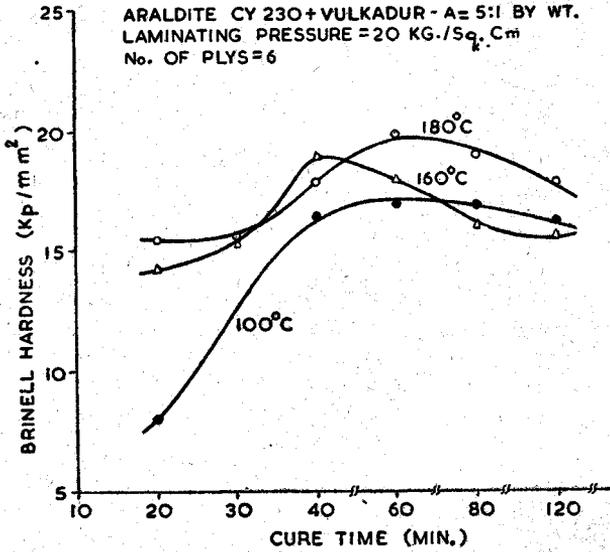*The bands at 860 cm.[-1] and 910 cm.[-1] were attributed to epoxy group.

FIG 2—Variation of Brinell hardness with cure time at various temperatures for glass fabric epoxy resin composites.
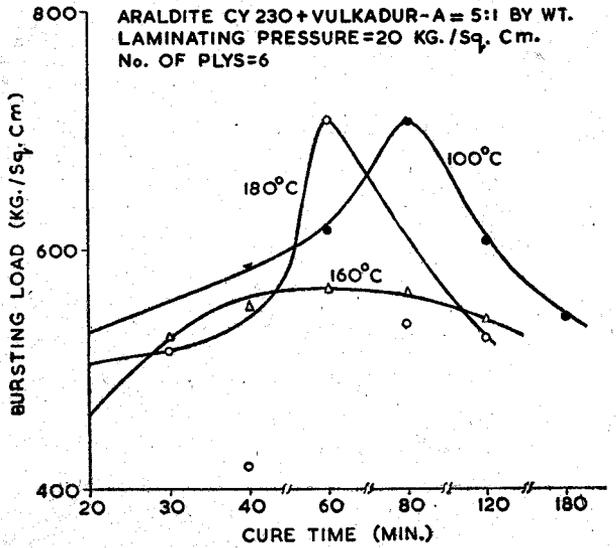

FIG 3—Variation of bursting load with cure time at various cure temperatures for glass fabric epoxy resin composites.

are practically the same and they occur almost at the same cure time at each temperature and, as is expected, the optimum cure time is much greater at 100°C. The curves at 160°C, however, show a peculiar behaviour which may be explained thus :

The curing of the resin may occur in two stages. The second stage may involve some of the reaction products of the first stage and occurs appreciably at higher temperature. Higher temperatures also cause a degradation of the uncured resin. At 100°C, the second stage is almost absent, so it is only after prolonged heating that the finally cured mass is obtained. At 180°C, due to rapidly occuring second stage curing, the final product is obtained before the thermal degradation is appreciable. At intermediate temperatures, the degradation and the second stage curing proceed simultaneously with equivalent rates and that is why the properties are less developed and there is no maximum in the bursting load curve in Fig. 3. Other features are more or less similar to those reported in our earlier communication[1].

In case of carbon black filled stock, (Fig. 4) maximum tensile strength has been found with stock containing 2·5 parts of carbon black cured at 60 minutes as in case of unfilled one; but the value is higher than
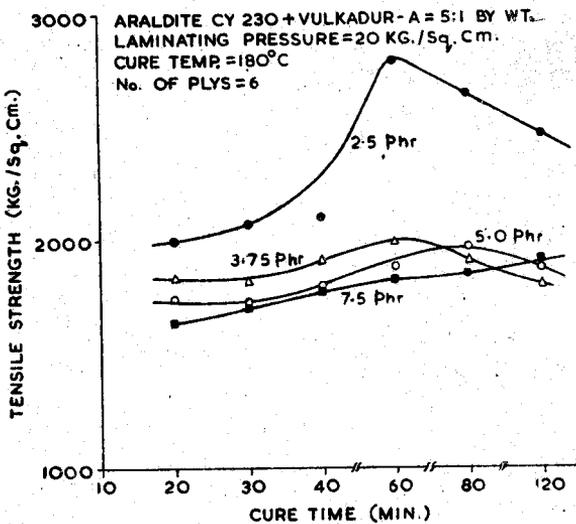

FIG 4—Variation of tensile strength with cure time for glass fabric epoxy resin composites containing different parts of carbon black (SRF) as fillers.
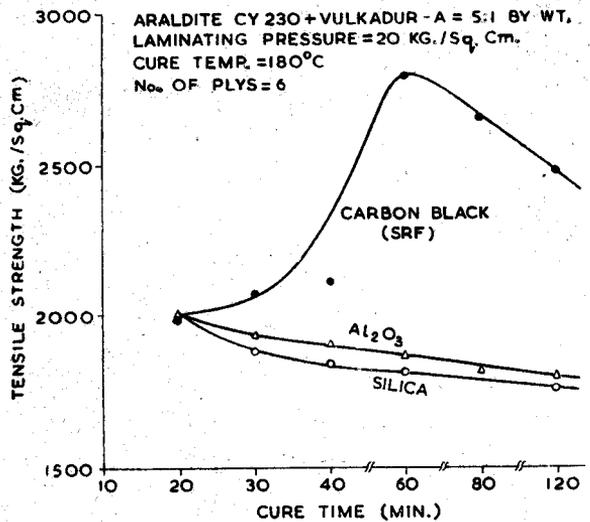

FIG 5—Variation of tensile strength with cure time for glass fabric epoxy resin composites containing fillers (Filler contents 2·5 phr).

that of the latter. Moreover, the fall in tensile strength after attainment of maximum is not so steep as in case of unfilled stock. It is also evident from Fig. 4 that as carbon black increases there is an overall decrease in tensile strength and its maxima shifts towards higher values of cure time.

The higher value of maximum tensile strength and its slow fall after attainment of maximum may be due to high surface activity of carbon black which causes stiffening of the polymer by holding two or more chains on their surfaces thus functioning as additional crosslinks. Further, its good dispersion in the resin matrix may facilitate transfer of stress to the neighbouring chains in the event of rupture of one chain resulting in high tensile strength values at optimum cure time and onwards. Moreover, it has been found by McGarry et al[2] that precipitated particles of elastomeric material, distributed throughout the crosslinked resin matrix in a fibrous glass reinforced epoxy resin composite, act as toughening agent against cracking. Carbon black with chemisorbed polymer chain on its surface may also be effective as a toughening agent to some extent against cracking in the composite as a whole. The increase in parts of carbon black increases the probability of getting unreacted carbon black particle in the composite, which causes many discontinuities in the resin phase as in case of non-black filled stock and thus it ultimately reduces the tensile strength values. The shifting of maximum tensile strength values towards higher cure time with increase in parts of carbon black in the composite is due to the fact that carbon black may have some retarding influence on the rate of cure and it increases with increase in its content in the stock. This retardation with $7 \cdot 5$ phr is so great that the maximum value in the curve is almost suppressed.

In case of stocks containing silica and Al_2O_3 as fillers as shown in Fig. 5, it is evident that tensile strength values fall from the very beginning in both the cases. This shows that the fillers are not reacting in any way with the resin matrix. Moreover, their mere presence produces many discontinuities in the resin phase.

In case of bursting load with stocks containing different parts of carbon black, Fig. 6, it is found that maximum bursting load values shift towards higher values of cure time with increase in carbon black filler content. This was also so in case of tensile strength (Fig. 4). The reason is same as discussed therein. Here, the steep rise and fall in all the cases unlike those of tensile strength clearly indicates that carbon black is a good reinforcing agent for the resin.

Bursting load values in case of stocks containng Al_2O_3 and silica as fillers (Fig. 7) have been found to decrease at a rapid rate compared to fall in tensile strength values with the same stock (Fig. 5). This is obvious because bursting is much dependent on the resin matrix which contains many discontinuities due to presence of these inactive fillers in the composite.
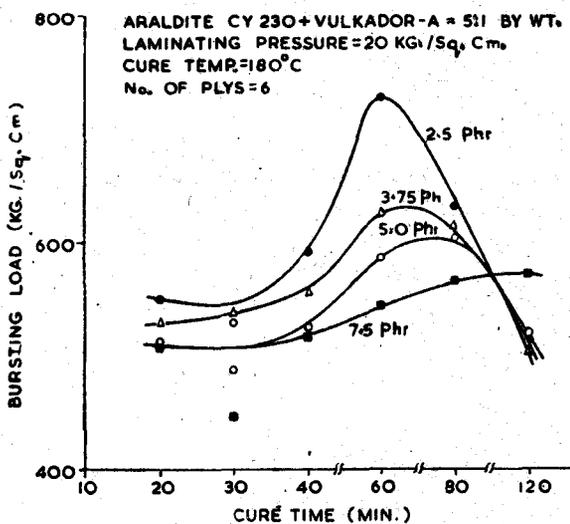
FIG 6—Variation of bursting load with cure time for glass fabric epoxy resin composites containing different parts of carbon black (SRF).
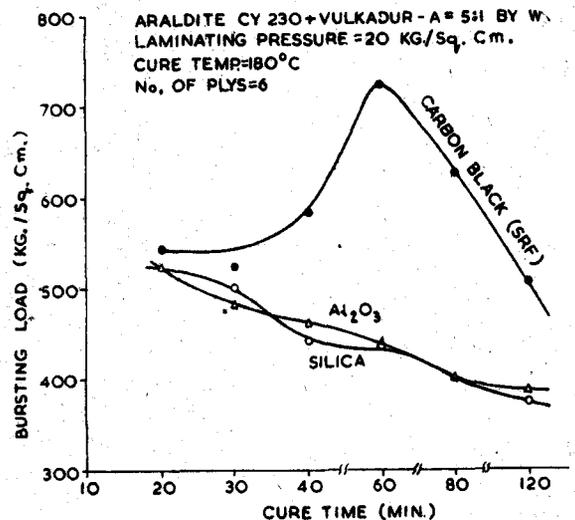
FIG 7—Variation of bursting load with cure time for glass fabric epoxy resin composites containing different fillers (Fillers contents $2 \cdot 5$ phr).
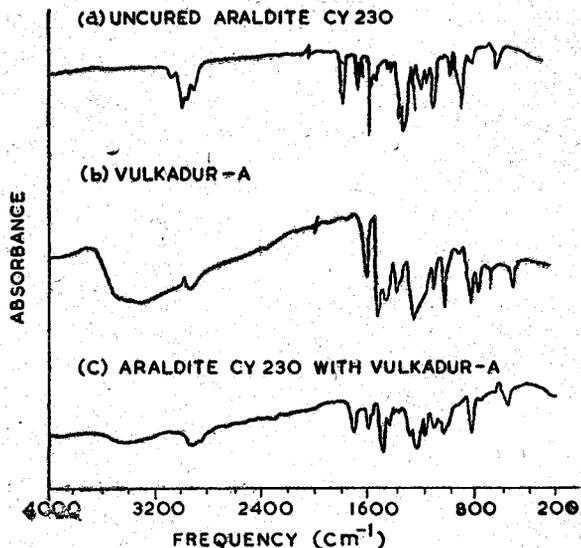
FIG 8—IR Spectrum of (a) uncured Araldite CY 230 (b) Vulkadur-A, and (c) Araldite CY 230 cured with Vulkadur-A, (cure time 20 minutes).
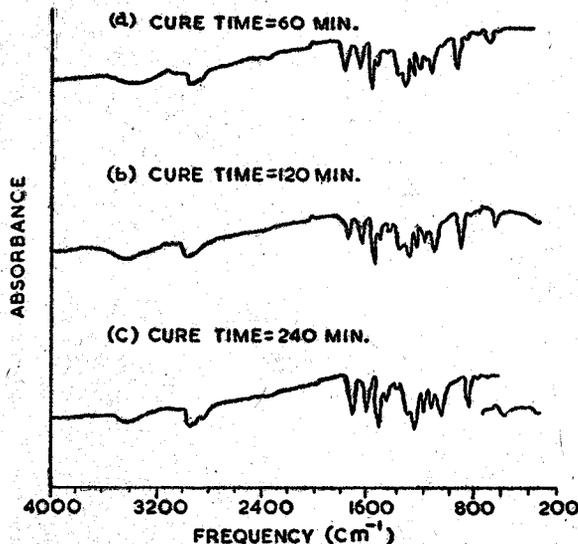
FIG 9—IR Spectra of cured Araldite CY 230 containing Vulkadur-A, cure time (a)60 minutes (b) 120 minutes (c) 240 minutes.

Spectral Analysis and Reaction Scheme

IR spectra have been taken in case of stocks cured at 100°C for different cure times (Fig. 8 & 9). It has been found that at 20 minutes of cure time almost all the epoxy groups are exhausted in addition to diminution of all other reacting groups. Incidentally, the tensile strength also becomes higher at 20 minutes of cure time. The reaction scheme as suggested in our earlier communication[1] correlates the mechanical data obtained with those from spectral analysis. The subsequent fall in tensile strength values upto 40 minutes of cure time may be due to partial breakdown of the products in addition to decomposition of the epoxy resin, leading to the evolution of gases like ammonia, methylamine and CH_2O and formation of methylene-bridged compounds. The evolved gases may also give rise to voids in the structure and thereby weaken it. The increase in tensile strength values from 40 minutes of cure time to 80 minutes of cure time may be due to formation of further cross-linked products[1]. The final fall after 80 minutes of cure time can be attributed to ultimate deterioration of the cured product. The steep rise in tensile strength at higher temperature and its earlier attainment of maxima and subsequent falling down is due to enhancement of the rate of cure and rate of deterioration at higher temperature.

CONCLUSIONS

Maximum values of tensile strength, hardness and bursting load have been found with stock cured at 180°C for 60 minutes of cure time (Fig. 1-3). The same maximum values of tensile strength and bursting load have also been found with stock cured at 100°C for 80 minutes (Fig. 1 & 3). In case of filled stock containing 2·5 parts of carbon black, it has been found that tensile strength and bursting load have increased. In all other cases there was deterioration in all the properties due to incorporation of fillers. It has been found that lower contents of carbon black have some reinforcing action whereas higher contents show some retarding effect on the overall curing process and reduce overall tensile strength and bursting load values. The superior performance of carbon black in lower proportion may be ascribed to the adsorption of resins on the surface acting as additional cross-linkings; but with higher proportion of carbon black or with other fillers, due to non-compatibility the fillers act as discontinuities in the resin matrix and thereby weaken it. Maximum tensile strength, hardness and bursting load values as found both in case of filled and unfilled stock are given in Table 2.

TABLE 2

MAXIMUM TENSILE STRENGTH, HARDNESS AND BURSTING LOAD VALUES FOR FILLED AND UNFILLED STOCKS

Stock	Tensile strength (kg/cm²)	Brinell hardness (kp/mm²)	Bursting load (kg/cm²)
Filled	2800·00	—	725·00
Unfilled	2585·00	19·89	703·10

REFERENCES

1. GHOSH, T. K. & BANERJEE, S., *J. Materials Sci.* London **8**, (1972), 915—923,
2. FREDRICK, J., MCGARRY & ANDRE M. WILLNER, Amer. Chem. Soc., Div. Polym. Chem., **8**, (1967), 2, 1056-53J