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Studies on glass-reinforced epoxy resin using either Vulkadur A or a mixture of Vulkadur A and triethanolamine as crosslinking agent

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Epoxy resin can be reinforced with glass (fabric form) using Vulkadur A (a phenol formaldehyde resin containing an hardening agent) as a crosslinking agent. Overall enhancement in mechanical properties has been observed with stocks cured with a mixture of Vulkadur A and triethanolamine.

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1. Introduction

In the design and fabrication of items made from GRP, knowledge of mechanical properties often becomes a factor of prime importance. From the published information, both in patented and literary form, it is understood that although much work has been done on the reinforcement of epoxy resin with glass (fibre, fabric or strand-mat form) in the presence of metal silicates, metal oxides, metal carbonates etc, as fillers and in the presence of materials other than Vulkadur A as crosslinking agent, almost no systematic study has yet been made on the mechanical properties of stocks cured with Vulkadur A as a crosslinking agent. In this work the effects of various parameters on the mechanical properties of the composites have been studied and chemical analyses of the cured product have been done with a view to correlating the mechanical properties with chemical changes occurring in the resin matrix.

2. Materials

2.1. Glass fabric

Plain weave E-type heat-cleaned* glass fabric has been used as reinforcing material in this study. The physical properties of the glass fabrics are given in Table I.

TABLE I Details of fibreglass cloth

Type of glass	E
Warp	60 threads in^{-1}
Weft	44 threads in^{-1}
Wt yd^{-2}	Approx. 4 oz
Design	Plain weave
Tensile strength of freshly drawn, undamaged fibre lbf in^{-2}	530 000

2.2. Resin

Araldite LY 533 (a laminating epoxy resin, DGEBA based) has been used as the resin and Vulkadur A and triethanolamine as the crosslinking agents.

2.3. Preparation of the varnish or resin solution

The resin and the hardener were taken in the ratio of 5:1 by wt in a beaker and mixed thoroughly until a clear homogeneous viscous liquid was obtained and diluted with acetone to a constant level.

2.4. Lamination

The laminates were fabricated by a hand layup technique and were cured in a big David Bridge curing press at a constant pressure of 20 kg cm^{-2}. To ensure complete removal of acetone the following procedure was followed.

After fabrication, the laminates were kept in air at room temperature for 1 h and dried in a vacuum oven at 40°C for 30 min. Moreover, during curing, after placing the laminates in the hot mould, and before giving final pressure, they were pressed and kept as such at the desired

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*Glass fabrics were heated in an oven for 6 to 8 h at a temperature of 300°C for removing the volatile components and starch-like material of the size applied to the fabrics during their manufacture.

pressure for 1 min. After that the pressure was released and final pressure was applied.

3. Testing

3.1. Tensile strength

Tensile specimens were machined to conform to the ASTM test method D 638, type 1 [1], and a universal testing machine has been utilized to obtain the tensile data. Rate of movement of the upper grip was 40 mm min^{-1}.

3.2. Bursting load

For measuring bursting load, specially-designed equipment as detailed in Fig. 1 has been used. A circular specimen of 2 cm diameter was placed over the copper gasket and the upper bolt was tightened over it. The whole thing was then fitted to the oil line of the high-pressure hydraulic booster and the oil pressure at which bursting occurred, was noted. A light liquid paraffin oil was used for this purpose.

3.3. Hardness

Hardness has been measured in a KM-02 hardness tester based on the Brinell principle. A steel ball of known diameter (5 mm), is pressed at known pressure (50 kg) against the specimen for a predetermined period of time (60 sec). The Brinell hardness is characterized by the area of the spherical calotte formed by the loading.

3.4. Chemical analysis

For the determination of epoxy values, a modified method used by H. Danbennerg and W. R. Harp [2] was employed. Total hydroxyl equivalent has been determined by using the acetyl chloride method [3] and phenolic hydroxyl has been estimated by titration as an acid in anhydrous ethylene diamine with standard sodium hydroxide solution [4].

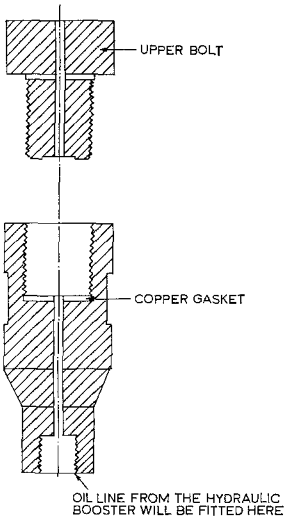


Figure 1 Sectional elevation of the equipment used for measuring bursting load (mild steel).

3.5. Crosslink-density

The crosslink-density was calculated by using the modified Flory-Rehner equation [5]. For determination of swelling, the method employed by H. Dannenberg and W. R. Harp [2] was used. The value of x, the polymer solvent interaction parameter, has been calculated from the slope of π/c versus c plot and been found to be 0.49. (As the resin is a commercial one and its composition is not definitely known, the accuracy of the value may not be very high.)

4. Results and discussion

The plot of tensile strength versus cure time (Fig. 2) shows that as cure temperature increases the maximum values of the tensile strength shift towards lower cure times. The initial slow rise in tensile strength at lower cure temperature range (85 and 100° C) may be due to slow curing of the resin but after 120 min of curing time the rate of cure is high. The overall decrease in the tensile strength values at 130° C may be due to formation of voids by the evolved gases resulting from the decomposition of hexa and some of the products of reactions. The increase in the tensile strength values at 150° C and further increase at 180° C may be due to secondary reactions (as suggested later) resulting in the removal of the evolved gases. At lower temperatures (85 and 100° C) the high tensile values may be due to curing of the Vulkadur A of the resin mixture through the formation of both ether and benzyl-ether linkage in addition to its normal curing with "hexa", leading to the formation of a complex structure having both secondary and tertiary amine bridges as detailed in the reaction scheme. It may be noted that since the resin is not pure, no attempt has been made to measure its glass transition temperature.

Fig. 3 shows that hardness is minimum with stock cured at 85° C and that it increases with increase in cure time. This lowering of hardness values at lower temperature unlike tensile values reveals the fact that hardness depends much upon the curing of the resin matrix. The

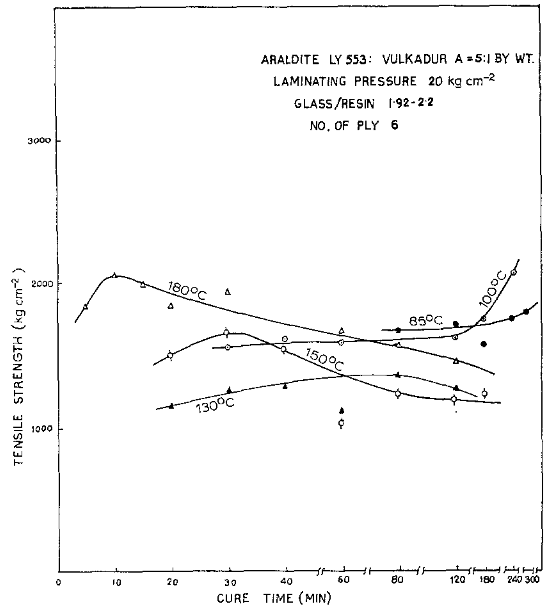


Figure 2 Variation of tensile strength with curing time at various temperatures for glass fabric epoxy resin composites.

overall increase in hardness at 100° C may be due to curing of Vulkadur A and shift of maximum hardness values towards lower cure time as cure temperature increases, is due to the increase in the rate of cure with increase in cure temperature.

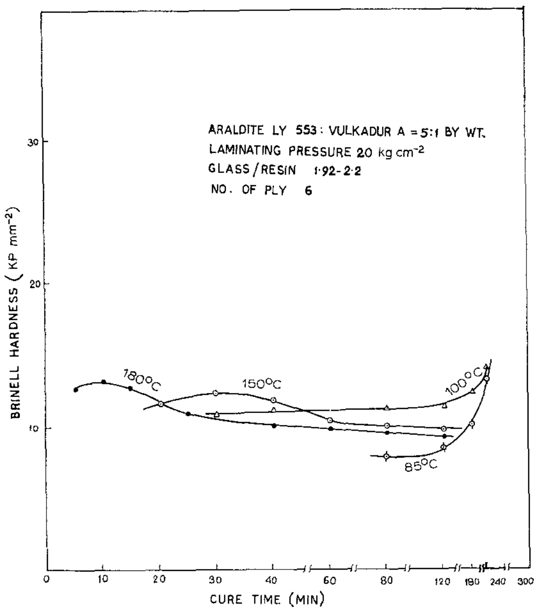


Figure 3 Variation of Brinell hardness with curing time at various cure temperatures for glass fabric epoxy resin composites.

The plot of bursting load versus cure time is similar to the tensile plot. The high values of bursting load at lower cure temperature (85° C) is due to complete elimination of voids, particularly in the interior of the composite (voids may arise due to evolution of moisture as a result of curing of Vulkadur A and due to entrapped air) by improperly cured resin mass lying in the interior of the composite, obtained probably by reaction of epoxy with Vulkadur A or by the uncured epoxy resin itself (Fig. 4). Now as the cure temperature increases, the probability of the occurrence of voids increases since curing of Vulkadur A itself, as also the curing of epoxy resin with Vulkadur A, lead to formation of gases such as ammonia, water vapour, etc, which obviously increase with increase in temperature, resulting in an ultimate decrease in the bursting-load values at higher temperatures.

Fig. 5 shows the plot of tensile strength versus glass/resin ratio. The tensile-strength value is maximum when the glass/resin ratio is 1.9 (by wt). The initial steep rise may be due to increase in glass-to-resin bond and filling up of the voids in the resin matrix by glass. The maximum corresponds to almost void-free stock and the final slow fall is due to insufficient resin content to cover up the voids inherent in the fabric base.

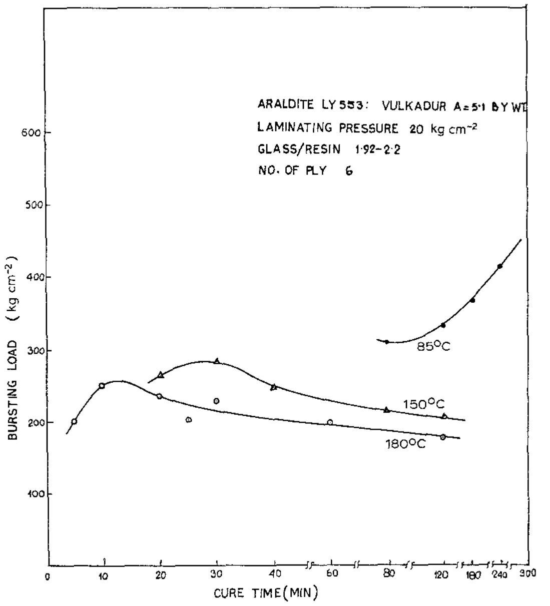


Figure 4 Variation of bursting load with curing time at various cure temperatures for glass fabric epoxy resin composites.

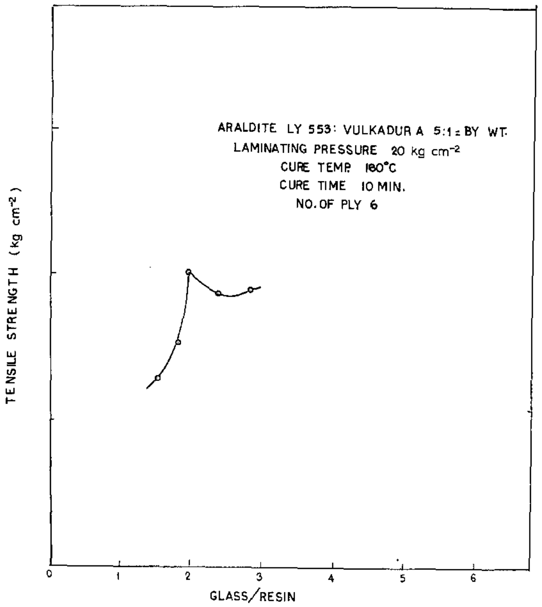


Figure 5 Variation of tensile strength with glass resin ratio for glass fabric epoxy resin composites.

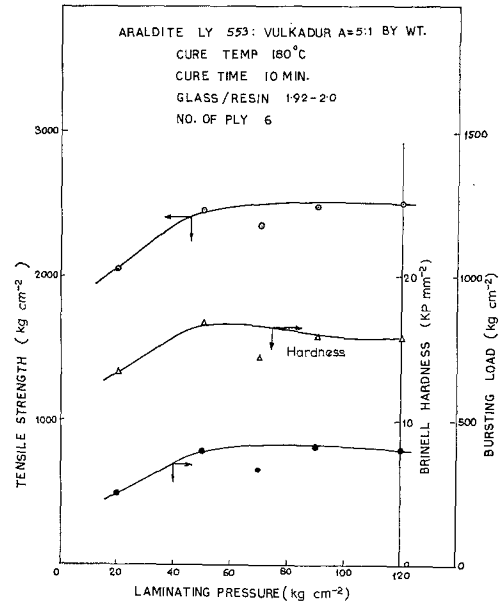


Figure 6 Variation of tensile strength, Brinell hardness and bursting load with laminating pressure for glass fabric epoxy resin composites.

From the plots of laminating pressure versus tensile strength, bursting load and hardness, it has been found that all three properties improve initially as laminating pressure increases from 20 to 50 kg cm^{-2} and from 50 kg cm^{-2} onwards up to 120 kg cm^{-2} the laminating pressure has practically no effect on the mechanical properties (Fig. 6). The initial rise in the properties arises from removal of air pockets inherent in the fabric base and air entrapped in the composite during fabrication, i.e., 50 kg cm^{-2} laminating pressure is just sufficient to give continuous structures free from voids arising out of the causes mentioned above.

Fig. 7 shows that as the number of ply increases, the tensile strength initially increases, reaches a maximum value and then remains almost constant after 8 ply. The lower value of the tensile strength with lower number of ply can be accounted for by realizing that the surface layers are defective due to the occurrence of crimps on the fibre and under lateral tension there is a possibility of separation of resin from the fibre in these weak spots, and thereby failure will be initiated at lower tension because the number of plys in the interior is not sufficient to compensate for the weakness. When the number of plys in the interior is sufficient, the weakness of the surface layer will be compensated for by the higher load-bearing capacity of these plys and from this point onwards the tensile strength will be independent of the number of ply. The decrease in the bursting-load values from the very beginning, as number of ply

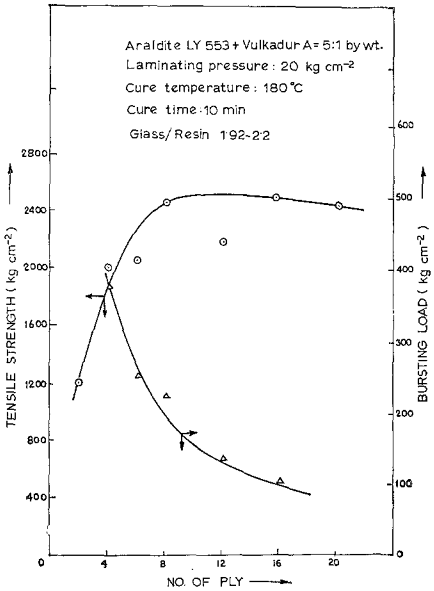


Figure 7 Variation of tensile strength and bursting load with number of ply for glass fabric epoxy resin composites.

increases is in sharp contrast to what has been observed in the case of tension. In the case of bursting load, the failure results from the application of a surface force, in contrast to the unidirectional lateral force in tension. The latter will not be so dependent on the existence of minute discontinuities in the resin matrix (in the form of voids etc.) as the former. The fast curing of Vulkadur A may lead to such discontinuities in the resin matrix. The possibility of occurrence of such defects, especially at the interior, will continuously increase with an increase in the number of ply and it may be due to this that the bursting load will decrease as the number of ply increases.

For the case of the increase in the resin content as shown in Fig. 8, the bursting load/unit thickness rises to a maximum value and then falls. The rise initially is slow but from about 33% resin content to 53% it becomes faster. As the resin content increases the thickness of the resin layer covering the glass surface increases. From the point at which steep rise occurs, substantial crosslinking in the resin matrix accompanied by good glass-resin bonding starts. The peak corresponds to maximum crosslinking with increased glass-resin bonding. The fall in bursting load when the resin content exceed 53% may be due to undercuring of the resin especially at the interior of the mass due to poor thermal conductance of the cured surface of the composite.

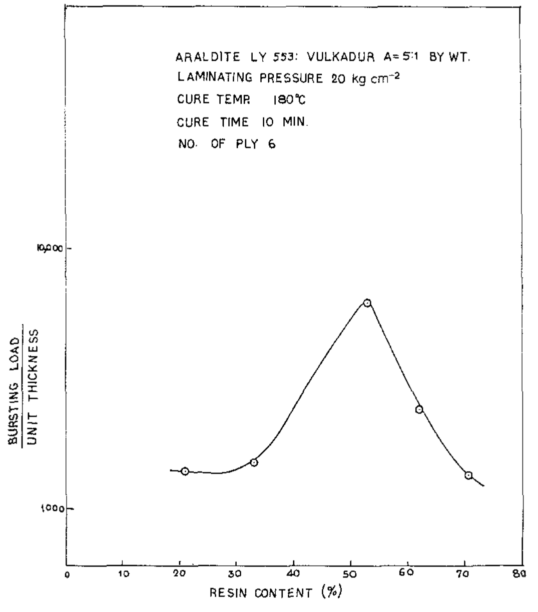


Figure 8 Variation of bursting load/unit thickness with resin content for glass fabric epoxy resin composites.

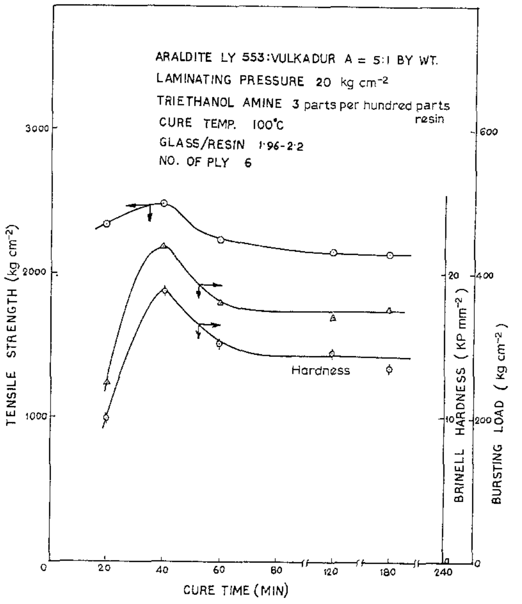


Figure 9 Variation of tensile strength, Brinell hardness and bursting load with curing time for glass fabric epoxy resin composites.

Fig. 9 shows the effect of cure time on the tensile strength, hardness and bursting load of stocks cured with Vulkadur A as crosslinking agent together with 3 parts per hundred parts resin (phr) of triethanolamine. From the figure it is evident that in all three cases there is an overall improvement in mechanical properties within the range of cure time studied as compared to those obtained with stocks cured with Vulkadur A only as discussed earlier. The increase in mechanical properties may be due to (i) curing of epoxy resin preferentially by triethanolamine and the hardener present in Vulkadur A without formation of any gas or vapour; (ii) curing of epoxy resin and Vulkadur A being catalysed by both the hardener and triethanolamine present in the system.

5. Chemical analyses and suggestion of a suitable reaction scheme

It has been found that epoxy-content decreases very rapidly up to 40 min of cure time at 100°C and then its decrease is very slow as evident from Fig. 10. At higher temperature, i.e. at

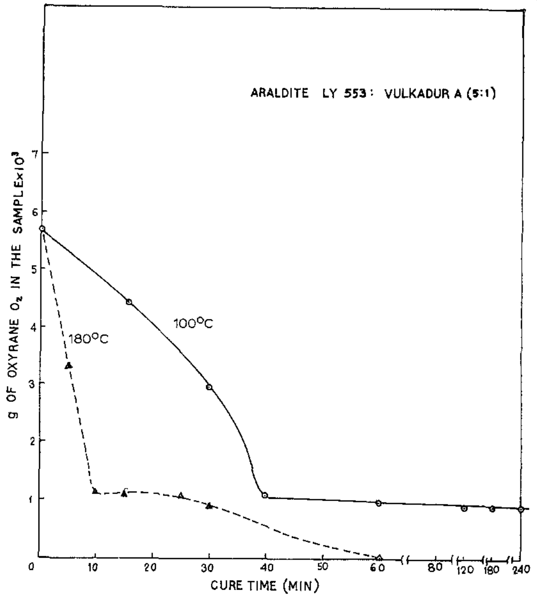


Figure 10 Variation of g of oxyrane O_2 in the sample with curing time at two different cure temperatures.

180°C the decrease in epoxy is much more rapid up to 10 min of cure and then the slow fall continues until almost all the epoxy groups have been exhausted after 60 min.

In the study of variation of phenolic hydroxyl content with cure time it has been found that with products cured at 100° C, phenolic hydroxyl content decreases slowly up to 180 min of cure; this is followed by a very steep decrease up to 240 min as is evident from Fig. 11. However, with stocks cured at 180° C initially, there is a decrease in phenolic hydroxyl content up to 10 min of cure and then the phenolic hydroxyl content remains almost unchanged up to 60 min and again from 60 min to 80 min there is a decrease in phenolic hydroxyl content.

The plot of total hydroxyl content, (*a*) versus, cure time (Fig. 12) shows that for the product cured at 100° C there is a rapid decrease in *a* with cure time (although up to 20 min the decrease is almost negligible). At 180° C the reverse effect occurs, i.e., up to 10 min of cure time there is an increase in *a* and after 10 min there is practically no change in *a* with increase in cure time.

Fig. 13 show the plot of crosslink density versus cure time. In the case of stock cured at 180° C, the maximum crosslink-density value corresponds to a 10 min cure as is evident from the figure. Incidentally, the mechanical properties also become highest in this period, but in the case of stock cured at 100° C, the maximum crosslink-density value has been found at 60 min though maximum values of the mechanical

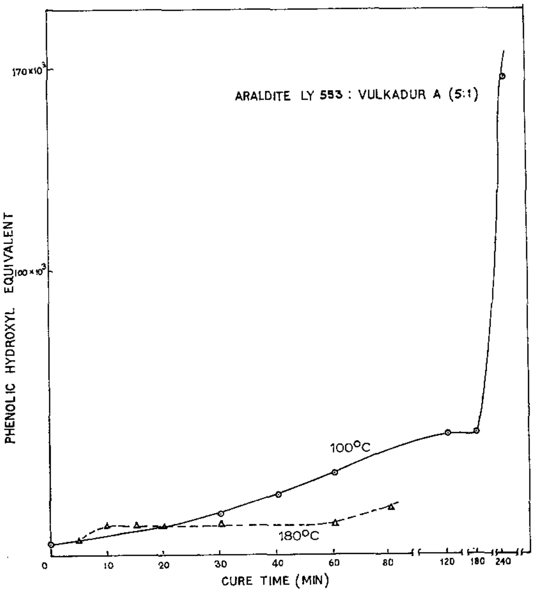


Figure 11 Variation of phenolic hydroxyl equivalent with curing time at two different cure temperatures.

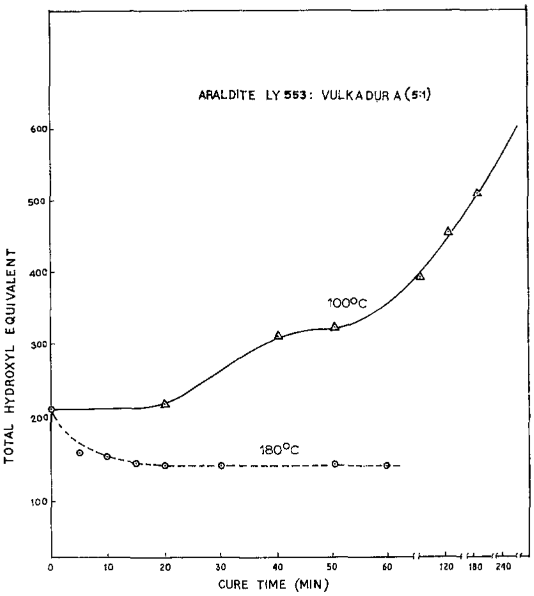


Figure 12 Variation of total hydroxyl equivalent with curing time at two different cure temperatures.

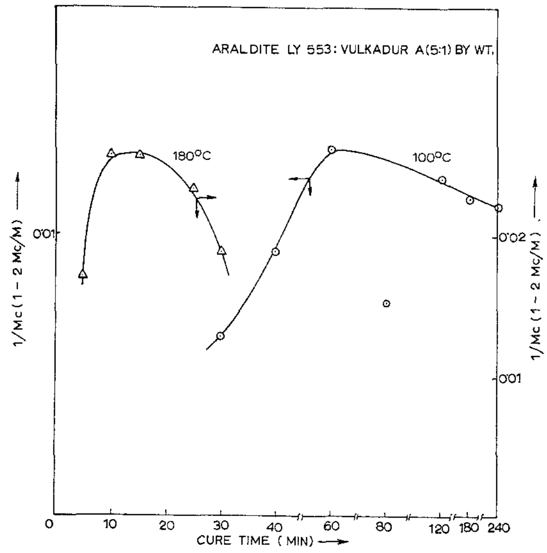
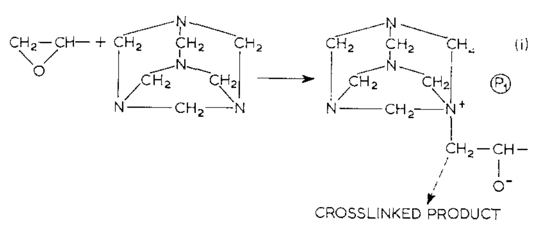
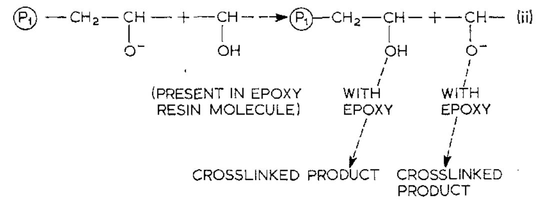


Figure 13 Variation of crosslink density with curing time at two different cure temperatures.

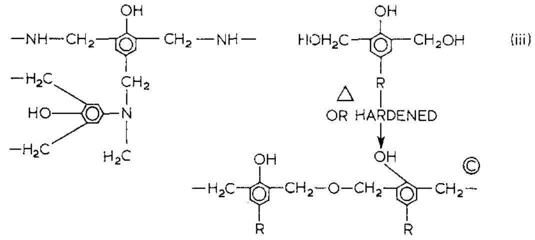
properties studied have been found with stock cured for longer time.

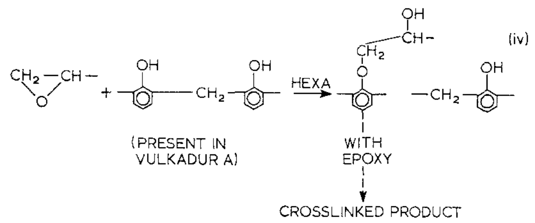
The results obtained from the study of mechanical properties and chemical analyses can be explained with the help of the following scheme of reactions. At 100°C the rapid decrease in oxirane oxygen (Fig. 10) up to 40 min of cure time and the attainment of maximum crosslink-density value after curing for 60 min may be due to the formation of crosslinked products from the reactions shown below.



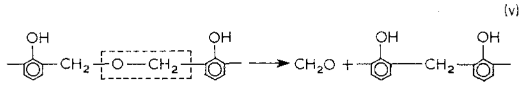


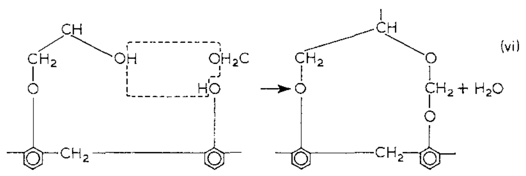
The following crosslinked products are also formed during hardening of Vulkadur A as reported earlier [6, 7].





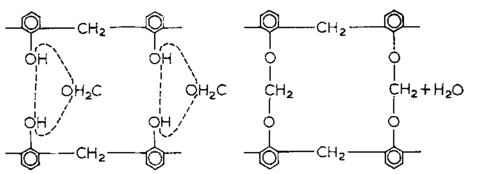
The high values in mechanical properties at lower temperatures (85 and 100°C) namely tensile strength, hardness and bursting load are due to reactions mentioned above leading to crosslinked products. After 120 min curing, the steep rise in tensile strength, steep fall in phenolic hydroxyl content, fall in total hydroxyl content and crosslink-density, may be due to the following reactions.





The steep rise in the tensile strength may be due to various other condensation reactions between epoxy, phenolic hydroxyl, alcoholic hydroxyl and formaldehyde groups resulting in chain extension.

At 180°C, the steep fall in oxirane oxygen up to 10 min of curing a slow fall in phenolic hydroxyl content, increase in total hydroxyl content, overall increase in tensile strength and increase in crosslink density may be due to rapid occurrence of reactions as given earlier at 100°C in addition to the following:



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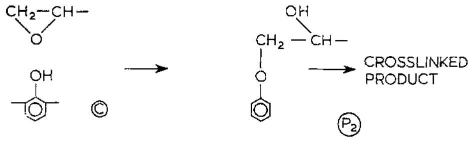
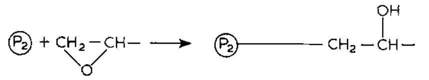


(viii)

The slow fall in tensile strength after a 10 min cure, constancy in total hydroxyl content throughout the range of cure time studied and in phenolic hydroxyl content up to 60 min curing time, slow fall in oxirane oxygen up to 60 min curing time and fall in crosslink-density, may be due to slow decomposition of all the products formed in addition to the following reaction



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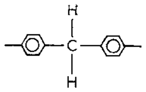
The initial increase in total hydroxyl may arise from the reaction of epoxy with active hydrogen derived from



present in Vulkadur A, or ammonia and water formed may also produce active hydrogen during the reactions.

At intermediate temperature, i.e. at 130° C, all types of reactions take place simultaneously leading to low crosslinked product having high void content due to evolution of gases like ammonia, formaldehyde and water vapour, resulting in overall decrease in tensile value throughout the range of cure time studied.

6. Conclusions

The tensile strength reaches a maximum with specimens cured for 10 min at 180° C and for 240 min at 100° C respectively. Maximum hardness has been found with stocks cured at 100° C for 4 h and maximum bursting load has been obtained with specimens cured at 85° C for 4 h. Tensile strength reaches a maximum at a value of 1.92 for the glass/resin ratio. Tensile strength, bursting load and hardness reach maximums at a value of 50 kg cm^{-2} for laminating pressure, and bursting load/unit thickness attains a maximum at a resin content of 53%. With increase in the number of ply, tensile strength initially rises and finally levels off at a nearly-constant value after 8 ply. At a fixed glass/resin ratio bursting load falls from the beginning with increase in the number of ply. Highest values of tensile strength, hardness and bursting load have been obtained with laminates cured at 100° C for 40 min cure time using Vulkadur A + 3 phr of triethanolamine as crosslinking agent. The following are the maximum values of the mechanical properties obtained with stocks cured with Vulkadur A and Vulkadur A + 3 phr of triethanolamine as crosslinking agent.

With Vulkadur A		
Tensile strength	2447 kg cm^{-2}	With specimen cured at 180° C for 10 min cure time at 50 kg cm^{-2} laminating pressure
Bursting load/ unit thickness	8130	With specimen cured at 180° C for 10 min of cure time having 53% resin content
Hardness	16·84 kp mm^{-2}	With specimen cured at 180° C for 10 min cure time at 50 kg cm^{-2} laminating pressure
With Vulkadur A + 3 phr of triethanolamine		
Tensile strength	2486 kg cm^{-2}	With specimen cured at 100° C for 40 min of cure time at 20 kg cm^{-2} laminating pressure.
Bursting load	438.3 kg cm^{-2}	
Hardness	18.61 kp mm^{-2}	

Lastly, it can be concluded that maximum crosslink density does not always correspond to maximum mechanical properties.

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