Comparison of the Effect of Curing on the Properties of E-Glass/Cyanate modified Epoxy Cross Plied Laminates

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Abstract High performance polymer composite laminates that are used in Aerospace and Electronics industries requires laminates that are structurally rigid besides exhibiting high stiffness and good di electrical properties. They are required to be transparent to EM waves in order to transmit the signal with almost zero transmission loss. Response of the laminates under different loadings could hence establish a potent material combination with high structural strengths that could be used in sectors dealing with Signal transmissions. The results thus acquired can be used as a database for choosing relatively better materials for Radome and their advanced versions in the coming decades. To augment this, thin laminates with 4 plies with simple stacking configurations of 0/90/0/90 degrees as applicable to a cross plied laminates were fabricated with cyanate ester modified epoxy resin and 1200GSM E glass unidirectional fiber. Flexural and Impact strength were the properties identified for the accessing the structural responses of the Laminate as against room and oven curing conditions. FESEM images were applied to validate the experimental findings.

Index Terms—Cross ply, Cyanate loading, Structural properties, Radome.
1. SCOPE AND OBJECTIVE:

This work attempts to identify the relative assessment of few critical properties pertaining to two laminates done with Hand Lay and Compression molded technique. Laminates were cured under Room and Oven curing conditions respectively (1-2). The Properties that were identified for the assessment were Flexural and Impact strength and further after which they were scanned for FESEM morphologies. A simple 4 ply, cross ply configuration was used for laying the laminate under both the curing conditions. Signal processing divisions with Radar installations in a variety of disciplines needs a cover to protect them, wherein optimized mechanical and Di electrical properties besides thermal and environmental properties are mandatory criteria’s. (3) Such covers called as Radome are made by these kinds of Laminates and a wide scope of developing them is a real possibility in the ever demanding high tech world of generation next Communication systems.

2. EXPERIMENTAL WORK

_**Laminate Fabrication.**_ The material and optimization of the curing agent Epoxy resin, curing agent and unidirectional fibers of 1200 GSM were procured from Sackthi fibre, Chennai, India and Bisphenol, the Cyanate ester was imported from Shangai Righton, Shanghai, China. Curing agent i.e., the hardener (Tetraethyleneamine), was optimized with regard to Cyanate ester resin (BACY) modified Epoxy resin (Di-glycidyl ether of Bisphenol A (DGEBA)). Optimization was done by varying the form, state and quantity of the curing agent, through number of trials till the defect free curing was observed in the resin mixture. Good potting period of around 15 to 30 minutes with zero defects was observed when 25.33% of the curing agent was mixed by uniform stirring for 10 minutes and later added to the blend of cyanate ester/Epoxy resin mix and allowed to cure. Before this optimization was achieved, defects like continuous foaming resulting sponginess in the cured blend, presence of glassy pin holes of varying sizes inside and open blow holes on the cured surface and presence of partially trapped undissolved cyanate were observed visually. On the addition of the un- optimized curing agent earlier and due to the obvious exothermic reaction, accelerated gelation of the blend was observed, thereby reducing the potable time of the resin mixture (6-7).

The laminate composites were initially fabricated from modified Epoxy resin loaded with 0%, 5%, 10% and 15% of Cyanate ester for Matrix and E-Glass unidirectional fiber of 410 GSM with four plies kept at the same symmetrical cross ply orientation of (0°/90°) reinforcement (8). Later after finding the optimized laminate from the above constraints, four more laminates of the same stacking configurations of (0°/90°)2 were made by Hand lay method using 1200 GSM unidirectional fiber. All precautions as per the ASTM guidelines were observed while fabricating the laminates.

Different types of loading were subjected on the specimen to find out the flexural and impact strength of the laminates. The Charpy impact test, also known as the Charpy V-notch test, was done in another apparatus consisting of a pendulum of known mass and length that is dropped from a known height to impact a notched specimen of material.

_Fabrication of Laminates and Testing._ A steel mould plate coated with silicone release agent and then a layer of resin was applied by a brush. The first layer of fiber (300X300 mm2) was placed on the resin and consolidated using roller. The process was repeated to construct four sets of 8 cross plied laminate with 0%, 5%, 10% and 15% of cyanate loadings. Four of the Laminates were cured at room temperature and were then demoulded after 10hours. And another four were compression moulded and latter oven cured. Using ASTM standards and by water jet cutting, specimens were prepared. UTM of associated scientific
Engg. Works, New Delhi, India, with a maximum testing load rate of 5 ton with a digital encoder with built up software of FIE make was used for performing the flexural tests. The speed of the testing was the relative to the rate of motion of the grips on test fixtures during the test. The grips were tightened evenly and firmly to prevent any slippage. The speed of testing was set at the proper rate and the machine was started. Specimens were subjected to different loading to find out the flexural Strength of the laminate. The Charpy impact test, also known as the Charpy V-notch test, was done in another apparatus consisting of a pendulum of known mass and length that is dropped from a known height to impact a notched specimen of material.

3. MATERIAL CONSTITUENTS OF THE LAMINATE
- Unidirectional Fiber 1200 GSM
- Epoxy blended with cyanate ester
- Hardener (Tetraethyleneamine)

4. METHODOLOGY
The very first and foremost step, before starting to prepare the laminate was to optimize the hardener. The 4, cross plied and balanced laminates were fabricated by using an optimized amount of cyanate ester (15%, found through number of trials). The laminates were put in compression molding (4) for 1 hour at 120\(^0\)C and further at 180\(^0\)C. Here the air pockets, structural voids, pores, etc. are removed due to pressure acting on the laminate. Compression allows the laminate to get pressed so that excessive amount of the resin blend flows out facilitating even distribution of liquid matrix material /resin. By eliminating the formation of voids and shifting of reinforcing fibers during the compaction process of the compression moulding, results in favorable changes of properties in the finally cured composites.
5. ROOM AND OVEN CURING
Out of the eight samples, four were room cured and the other four were oven cured. The samples that were cured in convection oven were maintained at 2200°C for two hours. After completion of two hours, samples were let to get cooled at room temperature. As a result of curing at elevated temperature the colour of composites turn yellowish or brownish. (5) Some of deformation like slight bending of the laminates was observed due to the relative thinness of the laminate.

6. TESTING AND CHARACTERISATION

Mechanical Test.

Flexural Properties. The flexural strength of a material is the strength value of resistance under bending deformation. For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength.

In a three-point flexural testing apparatus load is applied by one supported beam to the center of the specimen. In this study, flexural strength test is performed according to ASTM D 790-03 with three-point test apparatus.

Impact strength is the ability of material to withstand impact loading and it gives an idea about the brittleness of material. This property is determined by impact strength testing, measuring energy absorbed by material over a short period of time.

Figure 4: Few of the Flexural and Impact test specimens

Figure 5: Samples of Compression Moulded Oven Cured

Figure 6: Samples of Compression Moulded, Room Cured
7. PROPERTY VARIATIONS OF THE OVEN AND ROOM CURED LAMINATES

Table 1 Oven Cured

| Test Oven Cured | Unidirectional +Epoxy+0% +Cyanate Ester | Unidirectional +Epoxy+5% +Cyanate Ester | Unidirectional +Epoxy+10% +Cyanate Ester | Unidirectional +Epoxy+15% +Cyanate Ester |
|-----------------|-----------------------------------------|----------------------------------------|------------------------------------------|------------------------------------------|
| Flexural Strength (KN) | 0.570 | 0.625 | 0.90 | 0.950 |
| Impact Strength (Joules) | 7.7 | 8.4 | 10.3 | 10.2 |

Table 2 Room Cured

| Test Room Cured | Unidirectional+Epoxy+0% +Cyanate Ester | Unidirectional+Epoxy+5% +Cyanate Ester | Unidirectional+Epoxy+10% +Cyanate Ester | Unidirectional+Epoxy+15% +Cyanate Ester |
|-----------------|----------------------------------------|----------------------------------------|------------------------------------------|------------------------------------------|
| Flexural Strength (KN) | 0.120 | 0.050 | 0.125 | 0.750 |
| Impact Strength (Joules) | 3 | 3.9 | 5 | 10.8 |

Figure 7: Cyanate Vs Flexural Strength Oven Cured Room Cured

Figure 8: Cyanate Vs Impact Strength
CONCEPTS OF FESEM
The field emission scanning electron microscope (FE-SEM) is an analytical device used for investigating the surface of the samples through scanning. The scanning takes place by utilizing high-energy beam of electrons, these electrons are shot using a field emission gun. The sensitivity of this equipment is appreciably high when compared to the emission of tungsten filament it has 1000 times more power to generate the emissions but this can be achieved only under high vacuum conditions.

The functioning of this emission occurs obediently when the electrons beam exit the electron gun restraining the transaction of these electrons by metallic apertures and magnetic lenses. At the end, the potentials of positive and negative are isolated within the microscopes by detectors pertaining to both the type of charge emissions. The morphology of the particles in our samples was studied by Nova 200 Nano Lab Field Emission Scanning Electron Microscope (FE-SEM).

IMAGES AND DISCUSSIONS
Mechanical test results of laminates in general are dependent on both the fibre and matrix characteristics (7). The other main factors influencing are the bonding effectiveness of the fibre and matrix in transferring the loads and the laminate geometry of the composite panel. When it comes to the flexural test, the maximum tensile strength of the fibres present at the outer most layers of the laminate controls the strength and in the matrix front the polymer chemistry between the epoxy and the cyanate ester blend under the curing conditions play a decisive role in dictating the properties. When comparing the plain epoxy and cyanate ester modified version of the epoxy laminates, the latter is bound to show a higher value owing to increased toughness provided by the cyanate ester due to a higher cross linked density because of the formation of a network structure between cyanate ester and the epoxy matrix. Moreover, when the laminates are oven cured the cyanate increases this cross link density further.

Impact strength of the laminate is also influenced by the degree of toughness of the laminate in general and this also varies under room and oven curing conditions. As discussed above the main factor here will be the role played by the matrix chemistry besides to some extent the fibre geometry and the laminate configurations. The higher cross sectional area of the fibre besides the ability to behave in a ductile way by the laminate under the sudden loads could possibly decides the resultant impact strength.

The above discussions based on the theoretical concepts and earlier research works have been found to be proven under the present investigations.
The validations in terms of the FESEM images have been discussed as below:

In flexural under oven cured conditions, the higher magnification of 1000x to 1200x clearly shows few fibres getting broken in the outermost layers with elongated cross linked fibres in the inner layers in the cross plied layers of the laminate. Under lower magnification the straight line fracture with minimum bristles with almost a perfect resin coating are revealed as expected. Obviously the test also showed a value of 950 KN as against 750 KN under room curing conditions, shows a higher flexural strength for an oven cured specimen.

The presence of straight line mode fracture at the peripheral layers depict a relatively a fast brittle fracturing mode even under flexural loading. In the room curing conditions, under the higher magnifications, it is observed the presence of sheared matrix with not much fibre deformities. But the lower value of 750 KN is an indication of the underperforming cyanate under room temperatures. Though the matrix plays a second fiddle in load carrying task, the warp and weft nature of the observed cross linked fibres and a sheared resin could have played a role in bringing the value down.

Impact strength of the room cured specimen showed a higher value of 10.8 Joules than the oven cured one with 10.2 Joules. Though the cyanate ester enhances the strength better under a higher curing temperature by improving the toughness of the matrix, the presence of intact fibres, the main load bearers along the loading directions under the higher magnification besides the presence of a partially sheared resin coat under low and latter a completely removed resin coat at a higher magnification reveals ultimately a ductile mode of fracture to justify a higher value of the impact strength for the room cured specimen.

8. OVEN CURED SPECIMEN /FLEXURALTEST/ ESEM IMAGES UNDER DIFFERENT MAGNIFICATIONS:

![Figure 12](image12.jpg)  ![Figure 13](image13.jpg)

![Figure 14](image14.jpg)  ![Figure 15](image15.jpg)
Figure 12: Shows fracture bonding is linear in nature typical of brittle fracture. The fibre have cut with least bristles and no resin coating found flawed.
Figure 13: Higher magnification shows, the presence of spokes in the inner layer after fracture. However, the outer surface shows a (straight line) fracture typical of brittle fracture. The lower typical impact value is in correlation with the fracture nature.
Figure 14: Shows the top layer with the dominant resin layer that has fractured, and the inner layer shows the elongated fibre cross-linking.
Figure 15: Similar to the above but at the higher magnification of 200X showing the existence of fibre cross-linking.
Figure 16: Higher magnification of SEM at the inner fractured zone shows the cross linked fibre almost intact. The sandwiched fibre remains intact except elongated in the direction of force.
Figure 17, 18 and 19: The higher magnification of the fracture shows few fibres that have been cut at the peak load.

9. OVEN CURED SPECIMEN /IMPACT TEST/ FESEM IMAGES UNDER DIFFERENT MAGNIFICATIONS:

Figure 20: The SEM image shows the fracture edge with fine finished surface of the resin. The fracture is brittle type as under 40X.
Figure 21: Shows the fracture edge of the sample with dominant resin surface with no fibers observed. The magnification is 75X.

Figure 22: Shows the fractured zone with fiber free location and only resin mixture is seen at 160 X.

Figure 23: This fractured zone at 500 X shows the alternate layers of sandwiched fiber with resin. Figure 24: Shows the same at higher magnification.

10. ROOM CURED SPECIMEN /FLEXURAL TEST/ FESEM IMAGES UNDER DIFFERENT MAGNIFICATIONS
Figure 25: Shows fracture lines in the clear presence of fibers in the sub surface. Magnification here is 50X.

Figure 26: Similar to with top resin surface with brittle fracture. But the inner cross linked fiber not fractured.

Figure 27: Magnification at 250 X with alternate layers of cross linked fiber and resin alternate layers.

Figure 28: Same as but at higher magnification of 500X. With clear bonding of resin and fibers.

Figure 29: Same but at 1200 X showing the warp and weft of glass fiber cross linked.

Figure 30: Shows the resin layer and fiber. Resin sheared and fiber not sheared.

ROOM CURED SPECIMEN / IMPACT TEST/ FESEM IMAGES UNDER DIFFERENT MAGNIFICATIONS
Figure 31: Shows the fractured surface with dominant resins and partially deformed resins. The fracture not seemed to be brittle. Magnification 150X.

Figure 32: Magnification 35 X Shows the fractured surface with resin showing ductile type fracture and sub surface glass fiber elongated.

Figure 33: This image shows complete fiber Cross link with resin completely fractured and removed.

Figure 34: As above at 65 X.

Figure 35: As above at 150 X the fiber part intact along the loading direction without resin bonding.

Figure 36: As above at 270 X

11. CONCLUSION

The role played by Composites in the field of Aerospace and allied areas of Electronics is quiet significant. A variety of material properties could be generated owing to the anisotropic nature of the composite laminates. In the past few decades the emergence of Cyanate ester, as a high performance thermosetting resin is also being investigated and getting proven in many disciplines of Engineering. The investigation in our work with regard to the Cyanate blended epoxy resin in E glass reinforcement in developing Laminates with better structural related properties, like Flexural and Impact strength has been validated with FESEM analysis.

The performance of the laminate was found to be much better under oven curing conditions than room curing and the 15% addition of cyanate ester was also found to exhibit better properties.

Prediction of the laminate for the other properties and hence the overall response apart from these critical properties alone could very well make this particular type of laminate an eligible candidate and a potent structural material for many relevant applications.

Signal processing divisions with Radar installations in a variety of disciplines needs a cover to protect them, wherein optimized Mechanical and Electrical properties besides Thermal and Environmental properties are mandatory criteria's. Such covers called as Radome are made by these kind of Laminates and a wide scope of developing them is a real possibility in the ever demanding high technology world of Generation Next Communication systems.
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