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Influence of Curing Conditions on the Mechanical Properties of Silica-Phenolic Composites: A Comprehensive Study

Önder Güney[1, 3], Erdem Demirkesen[2]

Department of Metallurgy and Materials Engineering, Istanbul Technical University, Istanbul, Turkey [1, 2]

Nanokomp Advanced Materials Co. Ltd., Istanbul, Turkey [3]

Abstract: Determination of optimum curing conditions provides quality assurance in the production of high performance composite materials. To this end, many techniques have been developed for monitoring and controlling the variables of the curing process. In this study, the effect of several curing parameters, including curing temperature, curing period and curing pressure on the mechanical properties of silica-phenolic composites were investigated. Commercially available high silica fabric and a heat reactive, resole type phenolic resin (SC1008) were used in the production of composite laminates. After the impregnation step, the laminates were cured utilizing hot press under various cure conditions. The mechanical properties of the high-silica phenolic composite laminates were characterized in terms of tensile, combined loading compression, flexural and hardness (Shore D) tests. The densities and void contents of the composite laminates were measured using Archimedes principle. The results confirmed that both fibre and matrix dominated mechanical properties of the silica phenolic composites were affected by the curing process during composite manufacturing. Optimum curing conditions for this silica-phenolic composite system was determined as 1h at 165° C under a pressure of 8 bars.

Keywords: Curing Conditions, Silica-Phenolic Composites, Compression Moulding, Mechanical Properties.

I. INTRODUCTION

Over the past decades, polymer matrix composites have been widely preferred in various industrial applications due to their remarkable properties, including high strength to weight ratio, high stiffness and corrosion resistance. These properties are dependent on the selection of the suitable production techniques, as well as determining the optimum process parameters [1–3]. Among the process parameters, curing conditions have a substantial influence on producing highly cross-linked matrices, decreasing the residual stress and strain between the reinforcement and matrix materials, and reducing the void content in composite structure [4, 5]. Thus, several methods have been developed to establish optimum cure cycle to reach the desired structural performance [6-11]. Mechanical testing, is based on measurement of variations in a specific mechanical property by applying different cure regimes, is one of the most common and conventional methods used in the optimization of curing parameters [12–15].

The use of mechanical testing techniques in the optimization of curing processes has been preferred by many researchers. Lee and Springer [16] evaluated the dependence of the tensile, compressive and shear properties of the graphite-epoxy composites on various cure temperatures and periods. Gernaat [17] examined variations in the short beam shear (SBS) and combined loading compression (CLC) strength values of a commercial carbon-epoxy composite product at different isothermal curing temperatures. Wright et al. [18] analyzed the fracture toughness of polymethyl-methacrylate (PMMA) composites at different processing temperatures and periods, while Zhang et al. [19] tested the effect of non-uniform curing on the hardness of various locations within an epoxy plate. Tang et al. [20] investigated how the compressive and short-beam shear strengths of the unidirectional graphite-epoxy laminates are affected by the curing pressure. Liu et al. [21] revealed the changes in the tensile and interlaminar shear strengths of the carbon-epoxy laminates produced at different curing pressures. Despite this considerable effort devoted to assessing the relationship between curing parameters and mechanical properties of different types of thermoset matrix composites [12–25], there has yet to be any comprehensive study related the effect of curing processes on mechanical properties of silica phenolic composites.

The aim of this study is to determine the effect of variations in the curing parameters on the mechanical properties of silica-phenolic composites. For this purpose, temperature, time and pressure parameters were investigated to reveal the curing behavior in hot-pressed silica-phenolic composites. Tensile, compressive, flexural properties and the hardness (Shore D) of the composites were measured depending on the different curing regimes. To make an accurate comparison of the mechanical properties of the composites obtained under different curing conditions, density, fibre/matrix volume fractions and the void content of the specimens were also determined. Accordingly, the optimum curing conditions of silica-phenolic composites were discussed.

II. EXPERIMENTAL PROCEDURE

A. Materials

A commercial high-silica fibre fabric (KA-600P, Valmiera

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Glass Fibre JSC) with satin weave architecture was selected as the reinforcement material. Table 1 shows the specifications of the high-silica fabrics used in this work [26]. The matrix material was a heat reactive, resole type phenolic resin (SC1008, Momentive Special Chemical Company) having a viscosity of 2.4 P at 25°C. The density of the void-free casting of cured phenolic resin was 1.276 g/cm^3 [27].

TABLE I. Main specifications of the high-silica reinforcement (KA-600P)

Mass per Unit Area (g/m2)	600
Number of Threads (Warp/Weft)	19 / 13
Tensile Strength (N/cm) (Warp/Weft)	2000 / 1500
Density (g/cm3)	2.13
Thickness (mm)	0.55
Weave Type	1/7/8H Satin

B. Preparation of Silica-Phenolic Composite Laminates

The high silica fabrics were cut into 23 × 23 cm^2 sections using fabric scissors and the warp directions of the fabrics indicated with a marker pen. To achieve the ASTM standard thickness requirements [28–30], six layers of fabrics were sorted and initial weights of the fabric stacks were measured before the impregnation process. During the impregnation step, phenolic resin was applied to the high silica fabrics with the help of a brush and squeezing roller. Impregnated plies were stacked together in a warp aligned arrangement and dried in an oven maintained at 125°C for evaporating the solvent of the phenolic resin. After the drying step, high-silica phenolic laminates were placed between the preheated platens of the hydraulic press having a maximum capacity of 250 tons. The laminates were cured under various curing parameters that can be specified as temperature (125-205°C), time (0.5-24 h) and pressure (8-400 bars) in the press and cooled to room temperature at a rate of 2°C/min.

C. Characterization of Silica-Phenolic Composites

After the composite laminates were removed from the lamination plates, final weights of the composites were measured in order to calculate the weight and volume fractions of the matrix and reinforcement materials. Next, specimens for each mechanical test were prepared in accordance with ASTM specifications using a diamond wheel cutter. Essentially, a set of eight specimens from each laminate were selected per tensile, compression and flexural test to ensure repeatability and reliability of the mechanical test results. In all mechanical tests, warp direction of the fabrics was chosen as stress direction.

Tensile tests were conducted on an Instron 1195 model Universal testing machine having a 50 kN load cell and clip-on type single axis Instron extensometer with a 25 mm gauge length. Tensile strengths and modules of the composites were measured according to ASTM D3039/D3039M [28].Combined loading compression tests of the composites were performed with the same machine using a CLC test fixture, and the compressive strengths were determined as per ASTM D6641/D6641M [29]. Flexural tests were carried out utilizing a Shimadzu Autograph AG-X Universal testing machine with a 10 kN load cell. Flexural strengths and modules of the composites were calculated from stress-strain data obtained from the force-deflection curve. The support span to specimen thickness ratio of 32:1 was chosen as outlined in ASTM D7264-7264M [30]. The hardness values of the composite laminates were measured by a Type M durometer in accordance with ASTM D2240-05 standard [31]. For density measurements, at least three composite specimens were extracted from several regions of each laminate and the densities of the composite specimens were tested in water at 25°C using a dry/wet method (ASTM D792) [32]. Additionally, the void contents of the laminates were indicated by following the procedures stated in the ASTM D2734-09 standard [33].

III. RESULTS AND DISCUSSION

A. Effect of Curing Temperature

To understand the correlation between curing temperature and the mechanical properties of the silica-phenolic composites, composites laminates were cured at temperatures ranging from 125 to 205°C for 1 h under a pressure of 400 bar. Table 2 summarizes the average volume fractions of the constituents, the density, and the void content of the specimens produced at each of the cure temperatures.

TABLE II. Physical properties of the high silica phenolic specimens cured at temperature ranges from 125 - 205°C

Curing Temp. (°C)	Volume Fractions (%)		Density (g/cm^3)	Porosity (%)
	Fibre	Matrix		
125	46.75 ± 1.16	53.25	1.630 ± 0.008	1.80 ± 0.13
145	46.56 ± 0.28	53.43	1.633 ± 0.003	1.52 ± 0.15
165	47.59 ± 1.52	52.41	1.646 ± 0.010	1.28 ± 0.12
185	46.21 ± 0.98	53.79	1.636 ± 0.007	1.16 ± 0.12
205	47.06 ± 0.58	52.93	1.644 ± 0.004	1.15 ± 0.13

Two main results can be deduced from the table:

(1) Fibre and matrix volume fractions of the test samples produced at different curing temperatures (125-205°C) are almost constant ($V_f \approx 47\%$ and $V_m \approx 53\%$) and show good repeatability. It is well known that fibre/matrix volume ratio has a significant influence on the mechanical properties of the composites [3]. Therefore, the repeatability in the fibre/matrix volume fractions is crucial for ensuring the correct comparison and interpretation of the mechanical test results of the samples cured at different temperatures.

(2) The density values of the laminates did not change with increasing curing temperature, but void content decreased significantly up to 185°C. If the average fibre volume ratio of the laminates is assumed to be 47%, then the densities of laminates can be determined using the

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rule of mixtures as given in Equation 1 [34]:

$$\rho_c = \rho_f V_f + \rho_m V_m \quad (1)$$

where ρ_c is the density of the composite, ρ_f is the density of the reinforcement material, ρ_m is the density of the matrix material, and V_f and V_m are the volume fractions of the reinforcement and matrix materials respectively. By considering the reinforcement and matrix density values as given by the silica fabric and phenolic resin manufacturers [26,27], the theoretical density of the fully cured, void-free laminates was calculated as 1.677 g/cm^3. As shown in Table 2, this calculated theoretical density value is close to the measured density values (1.63-1.64 g/cm^3) of the laminates. The identical density values between the laminates cured at different temperatures is most likely due to the similarity between the densities of the fully cured phase and uncross-linked residual phase within the matrix structure. The decrease obtained in the void content with increasing curing temperature from 125 to 185°C is likely a consequence of a reduction in resin viscosity, which facilitates good fibre wetting.

The variations in tensile, flexural, compressive and hardness properties of the composite laminates under varying curing temperatures are given in Figi 1-3, respectively. With increasing curing temperature, tensile strength of the laminates increased from 162 to 176 MPa (Fig. 1), while flexural and compressive strengths increased from 212 to 276 MPa (Fig. 2) and 187 to 244 MPa (Fig. 3), respectively. As the curing temperature was raised from 125 to 205°C, the tensile modulus increased from 14.1 to 14.8 GPa (Fig. 1) and the flexural modulus increased from 13.9 to 14.4 GPa (Fig. 2). It can be seen from Fig. 3 that the hardness of the laminates increased from 80 to 90 between 125 - 165°C curing temperatures.

These results clearly show that curing temperature had a higher influence on flexural and compressive properties, than on tensile properties. This confirms that matrix dominated properties such as fibre/matrix interface strength and interlaminar bond strength are more sensitive to the flexural and compressive loadings [17]. Curing processes carried out at relatively low temperatures reduce both the rate of crosslink formation and degree of crosslinking [35]. The reduction in crosslinking results in weak bonding between the fibre/matrix interface and layers of the laminates, which reduces the mechanical performance of the composites. Whereas tensile and flexural modules, which are fibre controlled properties, are only slightly influenced by the curing temperature. The flexural and tensile modulus values are also compatible with each other. The increase in the hardness values of the laminates as a result of increasing temperature is mainly attributed to the complete curing of the resin. The test results show that the formation of crosslinking between the polymer chains improved the strength of the matrix material, which is a major property determining the flexural and compressive strengths. Mechanical test results also confirmed that at >165°C, the mechanical properties remained almost constant with higher curing temperatures. Therefore, 165°C can be selected as a suitable temperature for the curing process.

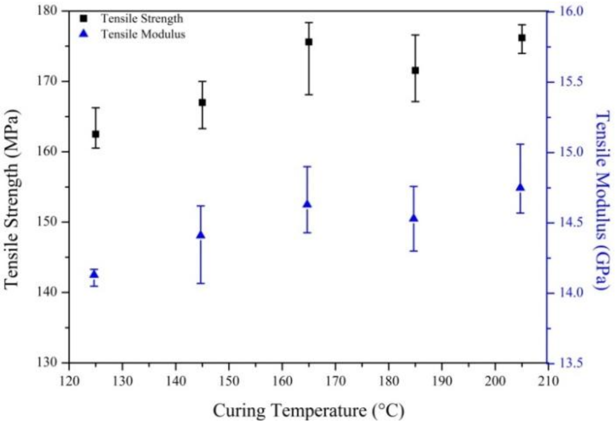

Fig. 1 Tensile strengths and modulus of the composite specimens cured at different temperatures

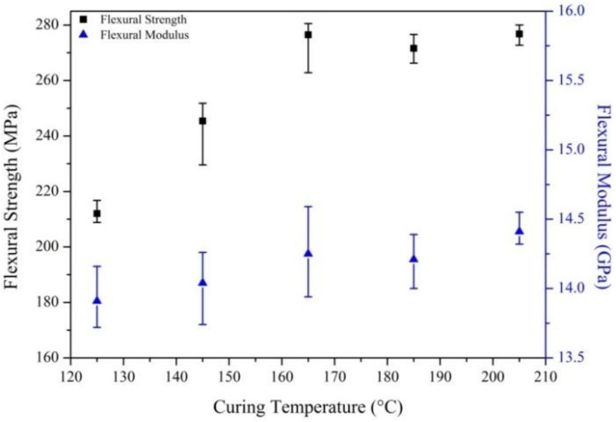

Fig. 2 Flexural strengths and modulus of the composite specimens cured at different temperatures

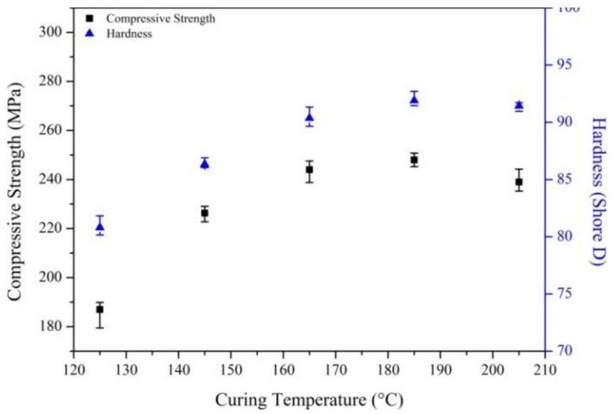

Fig. 3 Compressive strengths and hardness (Shore D) of the composite specimens cured at different temperatures

B. Effect of Curing Period

Since the optimum curing temperature was determined as 165°C, composite laminates were cured at this temperature for various curing times (between 0.5 to 24 h) to identify the influence of curing period on the mechanical properties of the silica-phenolic composites. The curing pressure was again maintained at 400 bars throughout the experiments. Table 3 illustrates the average volume fraction, density and void content of the high silica-phenolic composited cured for various time periods.

TABLE III: The average physical properties of the high silica phenolic specimens cured at 0.5 – 24 hours

Curing Time (h)	Volume Fractions (%)		Density (g/cm^3)	Porosity (%)
	Fibre	Matrix		
0.5	48.98± 1.07	51.02	1.656 ± 0.008	1.48 ± 0.16
1	47.59± 1.52	52.41	1.646 ± 0.010	1.28± 0.12
2	46.92± 0.79	53.08	1.642 ± 0.008	1.18± 0.10
3	46.85± 0.27	53.15	1.640 ± 0.020	1.27± 0.20
4	45.81± 0.70	54.19	1.632 ± 0.004	1.22 ± 0.13
5	47.31± 1.07	52.69	1.645± 0.006	1.21± 0.18
6	48.12± 1.03	51.88	1.652 ± 0.007	1.22 ± 0.12
7	46.31 ± 0.81	53.69	1.635 ± 0.150	1.28± 0.11
8	45.86 ± 0.60	54.14	1.632± 0.008	1.23± 0.15
24	46.00± 1.10	54.00	1.633 ± 0.010	1.24± 0.05

After 0.5 h, the change in curing time did not cause any substantial change in volume fraction, density and void content of the composites. The tensile and the flexural strengths of the high silica phenolic composites showed a slight increase when the curing time was increased from 0.5 to 1 h, while both strength values remained constant for curing times greater than 1 h (Fig. 4).

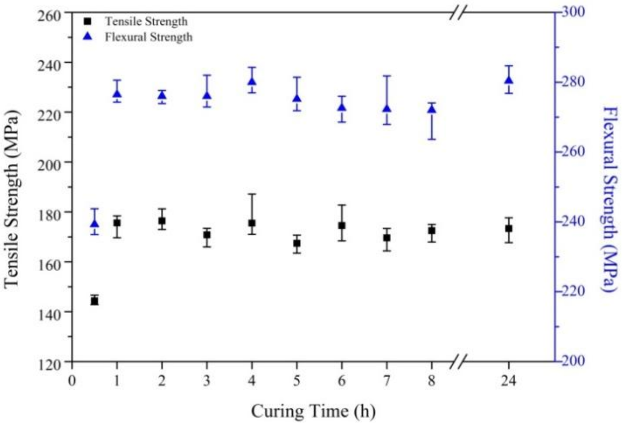

Fig. 4 Tensile and flexural strengths of the composite specimens cured at different periods

The average tensile and flexural strengths obtained for 1 and 24 h curing periods were 173 MPa and 274 MPa respectively.

Fig. 5 shows the compressive strength and hardness results for the curing periods. The compressive strengths were enhanced from 207 to 244 MPa as a result of increasing the curing time from 0.5 to 1 h. No significant change occurred in the compressive strengths of the laminates cured between 1 to 24 h. As expected, hardness values were only significantly changed between the curing periods of 0.5 and 1 h (Fig. 5). For curing periods beyond 1 h, the hardness of the composite laminates reached 90.4 ± 1.4. The hardness values did not change noticeably when the curing time was extended from 1 to 24 h.

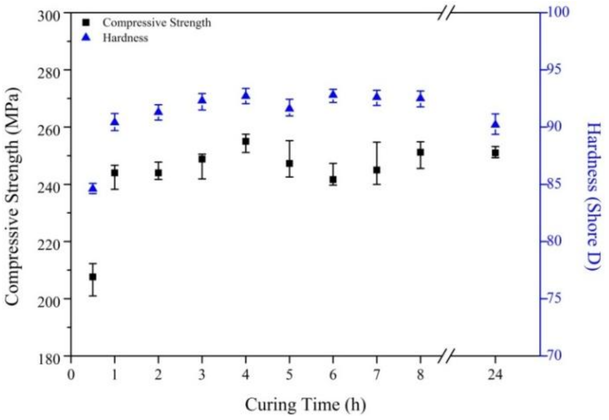

Fig. 5 Compressive strengths and hardness (Shore D) of the composite specimens cured at different periods

As a result, all mechanical tests confirmed that curing reactions took place during the first hour of the curing process: no significant increase was observed in the mechanical properties of the composites cured for more than 1 h. Therefore, 1 h was determined as the sufficient curing time for the high silica phenolic composites moulded at 165°C and under 400 bars.

C. Effect of Curing Pressure

To assess the influence of curing pressure on the mechanical properties of high silica-phenolic composites, laminates were cured at 165°C for 1 h at four different curing pressures. To provide the same pressure conditions as the industrial autoclaves used in aerospace industry, the minimum curing pressure was selected as 8 bar [1]. The maximum curing pressure tested was 400 bar. The average volume fraction, density and void content of the high silica-phenolic composites cured at varying pressures are given in Table 4.

The average volume fractions and densities of the composites are similar across the curing pressures tested (Table 4). This suggests that a curing pressure of 8 bar is sufficient for removing entrapped air and volatiles formed during the composite production.

TABLE IV: The average physical properties of the high silica phenolic specimens cured at 0.5 – 24 hours

Curing Pressure (Bar)	Volume Fractions (%)		Density (g/cm^3)	Porosity (%)
	Fibre	Matrix		
8	47.32± 0.893	52.68	1.646 ± 0.009	1.17± 0.064
50	47.43± 0.337	52.57	1.647 ± 0.004	1.18± 0.076
150	48.99± 0.737	51.01	1.660± 0.003	1.17± 0.260
400	47.59± 1.520	52.41	1.646 ± 0.010	1.28± 0.120

The variations in the average tensile strengths and modules of the composites with respect to curing pressure are presented in Fig 6. Increasing curing pressure did not affect either tensile strength or modules of the composite laminates up to 150 bar. When the curing pressure increased to 400 bar, the tensile strengths and modules of the composites increased to 175 MPa and 14.6 GPa respectively.

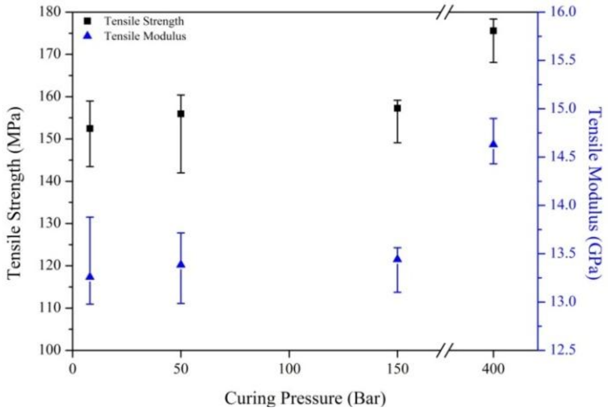

Fig. 6 Tensile strengths and modulus of the composite specimens cured at different pressures

This trend was also observed in the flexural strengths and modules of the composite laminates (Fig. 7).

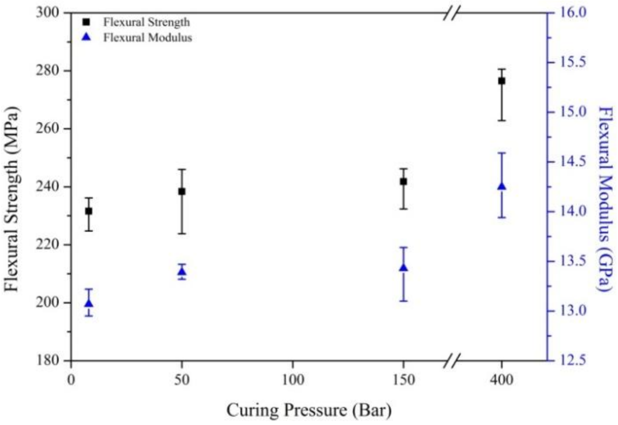

Fig. 7 Flexural strengths and modulus of the composite specimens cured at different pressures

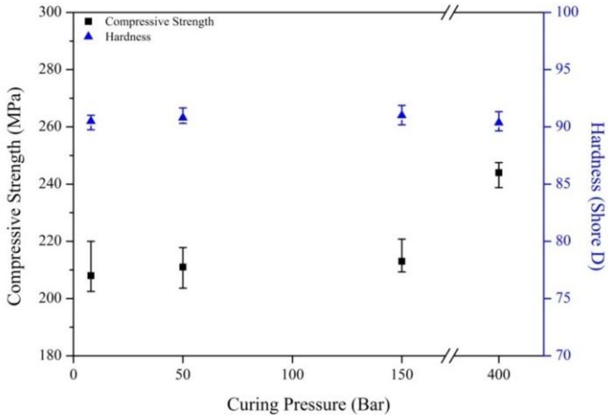

Fig. 8 Compressive strengths and hardness (Shore D) of the composite specimens cured at different pressures

As a result of increasing curing pressure from 150 to 400 bars, the flexural strengths of the composites increased from 241 to 276 MPa, and the flexural modulus increased from 13.4 to 14.2. As expected, no significant change occurred in the compressive strengths of the laminates cured at the pressures of 8, 50 and 150 bar (Fig. 8).

The maximum compressive strength value (244 MPa) was obtained at 400 bar. In contrast to all three mechanical test (tensile, flexural and compression) results, the hardness values (Fig. 8) of the composite laminates remained constant and appear to be independent of curing pressure. This is likely due to completion of curing process already at 8 bar, meaning that the hardness values of the laminates do not change significantly with increasing pressure (as the same cross-linking level is achieved for each pressure condition). The increase in strength values of the composites could be attributed to the efficiency of the resin flow, which might improve the bond strength between fibre/matrix interfaces and develop intimate contact between the layers of the laminates.

IV. CONCLUSION

The interest in high-silica phenolic composites rising from strategic point of view has contributed to the fact that the information about these materials is still difficult to obtain and even more difficult to interpret since most of the data have been restricted for a long time and their sources and quality cannot be ascertained in all cases. Therefore, the aim of the present study was to fulfil this gap and provide a comprehensive and easily accessible study about silica – phenolic composites for the first time in the literature. On the basis of the results obtained here, the following observations and conclusions can be drawn:

1) The appropriate curing temperature for this composite system was determined as 165°C, which is also in accordance with reports addressing the resin vendor for the E glass/phenolic system. At temperature above 165°C, no significant changes observed in mechanical properties.
2) A curing time of 1 h is sufficient for composite production. As evidenced by the mechanical test results obtained at longer curing times, no additional post-curing treatment was required.
3) The mechanical properties of the composites did not change between the pressures of 8 and 150 bar. This increase of pressure caused only a slight increase in the mechanical properties, suggesting that composites of optimum mechanical properties could be produced without the use of high pressures, such as autoclave techniques.
4) Change in curing conditions, like temperature, duration and pressure did result in any significant change to the fibre/matrix volume fractions, density or porosity of the composites, which facilitated the comparison of the mechanical properties in composite laminates produced under different curing conditions. In addition, the composite laminates had medium fibre volume fractions (40-50 %), as expected from the conventional impregnation technique applied.
5) The results obtained from this study can be utilized for processes (autoclave etc.) other than hot pressing for practical purposes.

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