

AB INITIO INVESTIGATION OF CARBON FIBRE REINFORCED PLASTICS APPLYING PHENOLIC RESINS

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SUMMARY: In this study, Carbon Fibres Reinforced Plastic (CFRP) was produced using simple gravity impregnation of 2D carbon fibre clothes with liquid phenolic resins. The study is aimed at revealing the influence of systematically modified raw materials and subsequently modified fabrication conditions on mechanical behaviour and structural morphologies of finished composites. Mechanical properties are obtained from bending tests and Thermomechanical Analysis while structural properties are obtained from optical and scanning electron microscopy. Emphasis is placed on such characteristics of used resins as viscosity, B-Time, solid content and free phenol content and their time dependence. Thermogravimetric Analysis and Differential Scanning Calorimetry of the resins were also carried out at various time intervals. Production variables as well as resin properties are found to have considerable influence on the structure and properties of finished composites. The investigations are part of a research project aiming at producing carbon-carbon (C/C) and carbon-carbon-silicon carbide (C/C-SiC) composites.

KEYWORDS: Fibre Reinforced Plastics, Carbon Fibre Reinforced Phenolic Resin, Phenolic Resin, Carbon Fibre Composites, Liquid Moulding Technology, Thermal Analysis, Flexural Strength.

INTRODUCTION

The high specific tensile strength and modulus of Fibres Reinforced Plastics (FRP), coupled with their enhanced toughness, excellent chemical and dimensional stability over a wide range of temperatures make them better alternatives to metals in many engineering applications. Carbon Fibres Reinforced Plastics (CFRP) for instance have a higher fatigue limit than most conventional metal structures and are consequently used in fatigue-critical components such as rotor blades in air- and spacecraft [1]. Polymer composites are particularly suited for multifunctional exploitation and are dominating the field of new multifunctional materials offering ability to sense, locate and even repair damage [2]. The attractive properties of FRP have been widely exploited in aerospace structures where weight reduction is a critical design consideration.

Despite the versatility and overwhelming potentials of FRP in virtually all facets of engineering applications is high manufacturing cost a major set back to their more widespread use. Making FRP components economically attractive through cost effective manufacturing

technologies has over the years continued to generate international research interest. This has yielded continuously improving composites technology which results in reduced cost and better performance. Apart from been identified as having the potential for overcoming the difficulties associated with medium to high volumes in the automotive industry, Liquid Moulding Technology has been used with successes for the manufacture of high quality stressed components in aerospace [3]. As a result of improved moulding technologies, applications of FRP is expanding and they are already finding widespread use as substitute for metals in the transport industry, building and civil engineering, oil and gas industry, medical implants and prosthesis among others.

Phenolic resins are well known for their excellent thermal and chemical stability and are widely used in composites manufacturing. Carbon fibres reinforced phenolic resins are generally used in rocket nozzle design. With the advent of space flight and ballistic missiles, phenolic resins have been successfully used in the ablative heat shield that protect the vehicle [4]. Phenolics produce low smoke and less toxic by-products upon combustion, and are therefore often used for applications in high fire risk areas such as aircraft interior panels where combustion requirements justify lower properties [5]. Besides phenolics have relatively high carbon yield and are commonly employed as carbon matrix precursors in the production of C/C composite materials for aircraft brakes [6]. The present study is aimed at evaluating the influence of resin characteristics and fabrication conditions on the structure and properties of carbon fibre reinforced phenolics produced using simple gravity infiltration of carbon fibres with liquid phenolic resins.

MATERIALS AND METHODS

Phenolic resins are produced by a condensation reaction between phenol and formaldehyde. The two common types of phenolic resin used in fibre reinforced composites production are novolaks and resoles. Resoles are produced by reaction between phenol and small excess of formaldehyde in the presence of either ammonia or caustic soda while novolaks is produced by reaction between a small excess of phenol with formaldehyde in the presence of an acid catalyst. Both are normally supplied as a fluid suspension with solid contents in the region 70-90% [7].

Three types of water soluble phenol-resoles (Type 1420, E95308 and E97783) supplied by Plastavis GmbH Berlin were used for this investigation. The resins were characterised with respect to viscosity, B-Time, solid contents and free phenol contents. These properties were determined for fresh resins and stored resins (stored at -20°C), a year after production, to elucidate their time dependence (Table 1). The thermal behaviour of the resins was characterised using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The equipment used was Netzsch STA 499 C. Samples of average mass 90mg were heated at $5^{\circ}\text{C}/\text{min}$ from ambient temperature to 1200°C in argon atmosphere. The rate of flow of the argon gas was maintained at constant value of $70\text{mL}/\text{min}$. Al_2O_3 was the reference material.

Dry 2D (0/90) woven carbon fibre clothes were laid up in an open metal mould. The resins were injected into the mould containing the woven reinforcing fibres under the action of gravitational force. Prior to impregnation, the mould was pre-heated to about 50°C to reduce the viscosity of infiltrating liquid thereby enabling a more rapid fill of the mould cavity. Cross linking reactions during curing of phenolic usually produce volatile materials which can result in voidy matrix. To avoid this, curing was carried out in an autoclave under high pressures. The cure samples were allowed to cool very slowly in the autoclave to ambient temperature.

Table 1 : Characteristics of applied water soluble phenol resoles

	Viscosity (20°C)	B-Time at 150°C	Solid content	Free Phenol content
Test method	DIN 53015	DIN 16916-02-C2	DIN 16916-02-HI	DIN 16916-02-L2
New				
1420	722mPaS	156s	73.3%	9.7%
E 95308	1100mPaS	70s	73.8%	4.8%
E 97783	1800mPaS	185s	80.4%	14.4
One year later				
1420	802mPaS	115s	72,1%	10,9%
E 95308	1125mPaS	65s	73,5%	4,8%
E 97783	2175mPaS	185s	78,3%	14,5%

RESULTS AND DISCUSSIONS

Investigations reveal no substantial change in the viscosity, B-Time, solid contents and free phenol contents of the resins a year after production. No significant alteration was also found in thermal behaviour of the resins.

Thermal Analysis of Applied Resins

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) indicate two-stage exothermic curing reactions for resins 1420 and E95308 with reaction exothermic peaks at 123°C and 148°C for resin E95308, 115°C and 150°C for resin 1420 (Fig.1). One stage exothermic reaction is observed for the curing of resin E97783. The reaction peak which is less pronounced than those for the other two resins occurs at about 130°C.

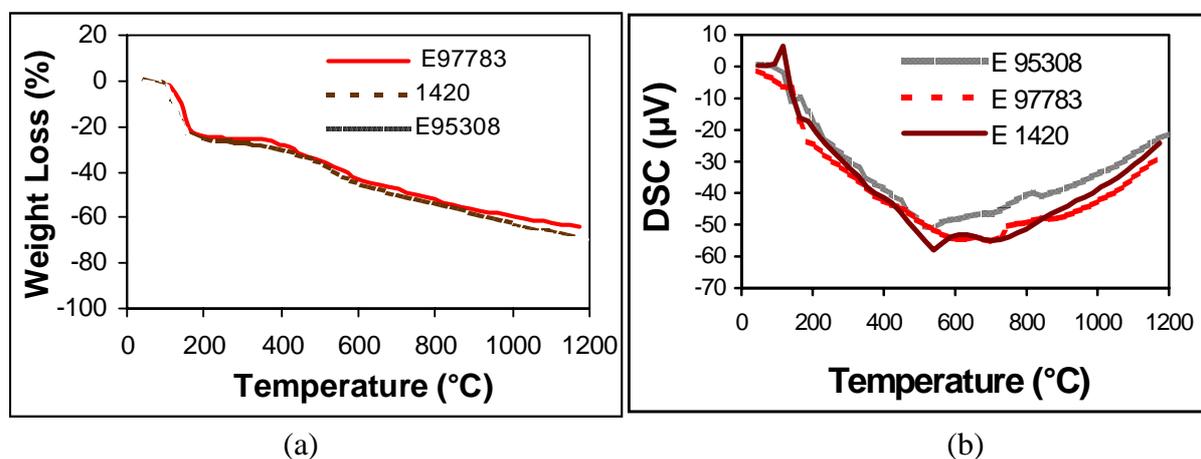


Fig. 1. Thermal Analysis of Applied Resins (a) TGA Profiles. (b) DSC Curves

Weight loss of resins when heated from ambient temperature to 1200°C occurs in 3 stages. The first stage occurs up to 350°C and involves condensation reactions during curing and subsequent evolution of carbon dioxide resulting in 31%, 29% and 25% weight loss for resins E95308, 1420 and E97783 respectively. Evaporation of water by-product during curing reactions accounts for greater amount of these weight losses. The second stage which occurs between 350°C and 600°C accounts for chemical decomposition and re-arrangement in resin resulting in evolution of low molecular hydrocarbons. Above 600°C, weight loss occurs at a much slower and steady rate. Evolution of hydrogen which remains the non carbon

constituents left in this temperature range accounts for this weight loss. All reactions are exothermic with varying reaction peaks depending on the characteristic of phenolic resin under investigation.

Microstructural Evaluations

Fig. 2 shows the representative optical micrographs of fabricated Carbon Fibre Reinforced Phenolics. The microstructures indicate high degree of impregnation of the carbon fibre cloth by the liquid phenolic resins. Wetting, fibre-matrix bonding, the amount and distribution of pores and shrinkage cracks in the finished composites depend on the characteristics of the applied resins and fabrication conditions. Void content (gas bubbles) of finished composites was evaluated using image analysis system. For samples produced from resin E97783, E95308 and 1420 at curing temperature of 120°C and under a pressure of 50bar, the porosity was determined to be 2.0%, 2.5% and 22% respectively.

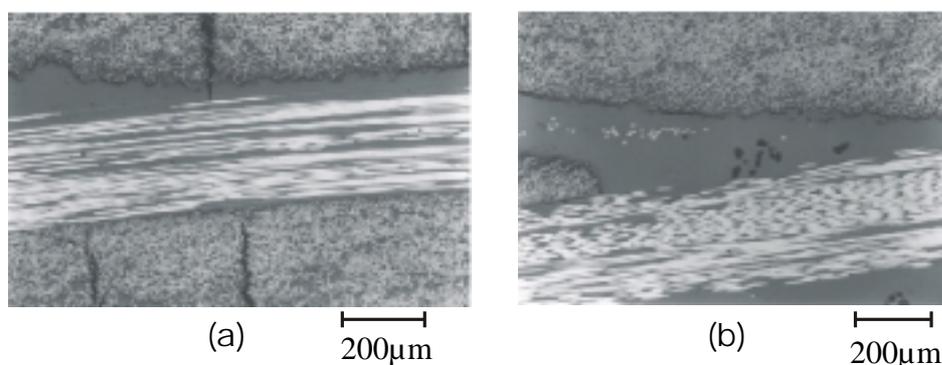


Fig. 2. Representative Photomicrograph of Carbon Fibres Reinforced Phenolic Resin Showing Shrinkage Cracks and Closed Porosity. (a) Matrix E 95308 (b) Matrix E97783.

Samples fabricated from 1420 contain large amount of uniformly distributed pores which are located both in the region between and within fibre bundles. Most of these samples shows very little or no evident of shrinkage cracks. Samples produced from E95308 on the other hand consist of matrix riddled with many and wide shrinkage cracks. There is no significant evidence of macro pores at the dense matrix regions of the composites. Scanning electron microscopy (Fig. 3) however indicates the existence of interfacial pores at the fibre matrix interface. The shrinkage cracks and porosity in samples produced from resin E97783 lie between these two extremes. Voids in these samples are made of clusters of small bubbles and are mostly located in the regions between fibre bundles. The cracks in the matrix are narrower and fewer than in E95308 samples.

The principal source of voids in the matrices of the composites are entrapment of air during mould filling, entrapment of volatile materials formed during cross linking reactions and dissolved gases in the resins. Poor wetting of the fibres by resin E95308 accounts for the interfacial pores in the composites produced from this resin. Scanning electron microscopy shows good interfacial bonding and wetting between matrices 1420, E97783 and the reinforcing fibres. Altering the chemistry of the carbon fibres' surface by exposure to boiling 70% HNO₃ for 2 hours have a deleterious effect on wetting and bonding between the carbon fibres and all the three applied resins. There seems to be no proven way to eliminate voids completely in Fibre Reinforced Plastics [8,9]. However, the presence of voids affects the mechanical properties of FRP and must be kept at the barest minimum. The void contents of

samples fabricated from resin 1420 are considered too high. Employing vacuum assistance which has been widely reported to be an effective means of reducing the porosity of FRP [8] could be employed to overcome the problem of porosity in matrix 1420.

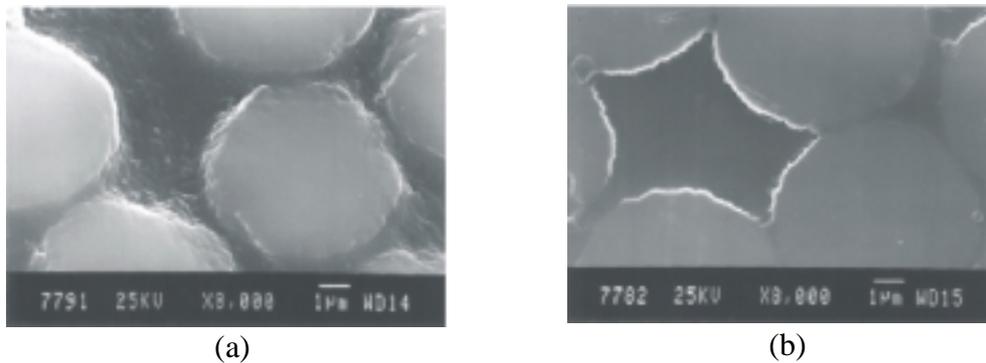


Fig. 3 Scanning Electron Micrograph Showing: (a) good wetting and bonding between fibres and resin E97783 (b) poor wetting and bonding between fibres and resin E95308.

Fig. 4 shows the dependence of closed porosity of the finished composites on the curing temperature. Volume fraction of pores decreases generally with increase in curing temperature. Previous studies have also shown a significant effect of impregnation and curing temperature on porosity of FRP [10,11]. Microstructural evaluations also indicate that the size and amount of shrinkage cracks increase with increasing curing temperature. This can be attributed to evolution of more volatile materials, hence more shrinkage, and increased thermal stresses at high curing temperature resulting in widening of cracks and generation of new ones. This probably occurs along the paths of clusters of bubbles thereby reducing the volume fraction of closed pores at high temperatures. Cracking was observed to continue in samples fabricated at high curing temperatures several hours after removal from the mould.

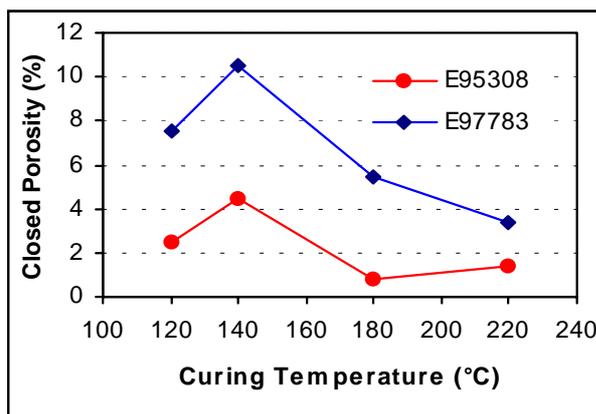


Fig. 4 Effect of Curing Temperature on Porosity.

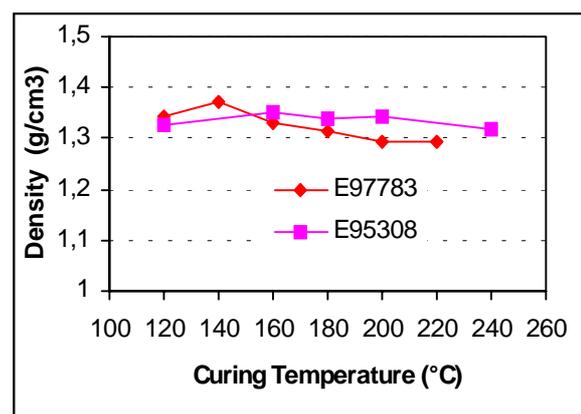


Fig. 5 Effect of Curing Temperature on Density.

This is applicable to all samples produced at high temperatures irrespective of the type of resin used. Such cracking was however noticed in all samples produced from E95308 irrespective of curing temperatures and they are much more intense and continue much longer than in the other two resins. The density of the samples were found to generally decrease with increasing curing temperature as shown in Fig. 5. The density decrease can be attributed to

increase in aggregate void content (shrinkage cracks and closed pores) of the composite as curing temperature is increased.

Thermomechanical Analysis

The dimensional changes in Carbon Fibre Reinforced Phenolics under additional load as a function of temperature was determined by Thermomechanical Analysis. The analysis (Fig. 6) shows modification in the expansion behaviour of the composite material as a result of the transformation taking place in the glass transition temperature range. The materials initially increase in length as temperature increases until a maximum temperature beyond which further increase in temperature result in reduction in dimension. This maximum temperature corresponds to the onset of glass transition. The maximum temperature as well as the expansion behaviour of finished composites are found to be largely dependent on type of resin used and the curing temperature. The change in length of the material was measured in two different directions for the same sample and it was discovered that the expansion behaviour is dependent on the orientation of the fibres. Investigations also show different expansion behaviour for cured resins without fibre reinforcement. The influence of the carbon fibre reinforcements therefore determines to a large extent, the thermal expansion behaviour of Carbon Fibre Reinforced Phenolics.

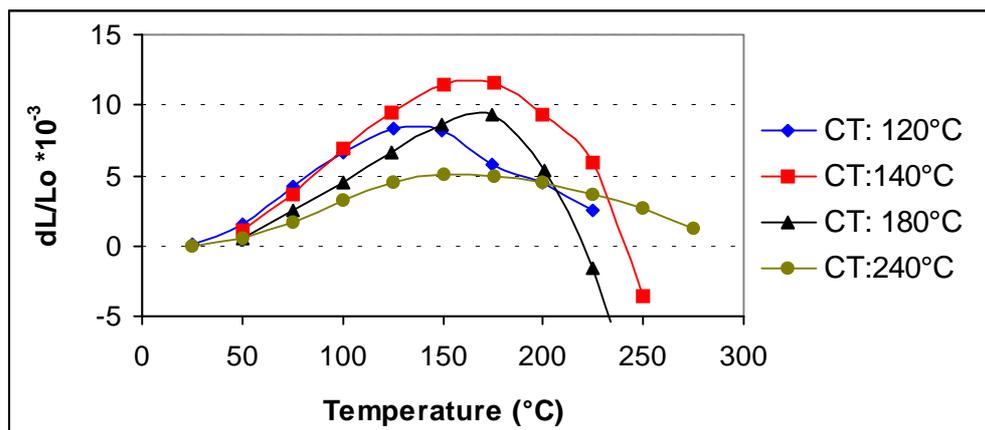


Fig. 6 TMA Curves Showing the Effect of Curing Temperature (CT) on Thermal Expansion Behaviour of Composites made from Resin E97783.

Flexural Strength

Investigations into mechanical properties of Carbon Fibres Reinforced Phenolics indicate that maximum flexural strength is achieved when the resin is cured at between 140 and 150°C. Fig. 7 shows that the flexural strength increases initially as curing temperature is increased and reached a maximum value at 150°C beyond which the flexural strength begins to decrease. However, significant drop in strength is not noticeable until curing temperature is in excess of 180°C. The lower strength at low curing temperatures can be attributed to an incomplete polymerisation reaction at this temperature for the given curing time. All the reactive groups are not consumed and the resins are not completely cured. As the temperature is increased, more reactive groups are consumed during curing resulting in more rigid cross linked network structure and more strength. Reduction in strength at higher curing temperatures is due to increase in the amount of shrinkage cracks in the matrix and possible deterioration of bonds between various reactive groups at high temperatures. Fig. 8 shows that

post curing of samples initially cured at 120°C at higher temperature lead to increase in strength. Increase in the amount of reactive groups consumed during post curing accounts for the observed increase in strength. Investigations also shows an increase in flexural strength of finished composites as curing pressure was increased between 15 and 50bar.

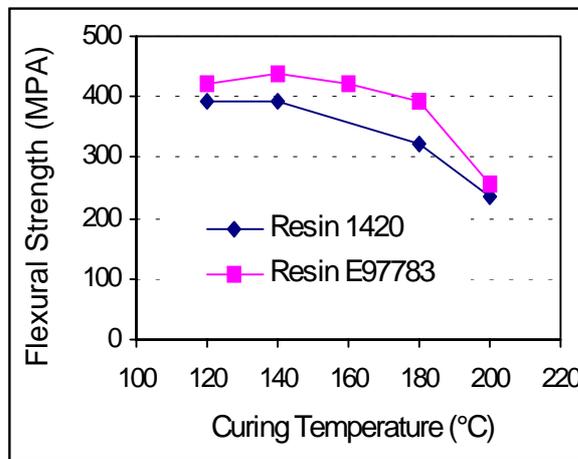


Fig. 7 The Effect of Curing Temperature on Flexural Strength.

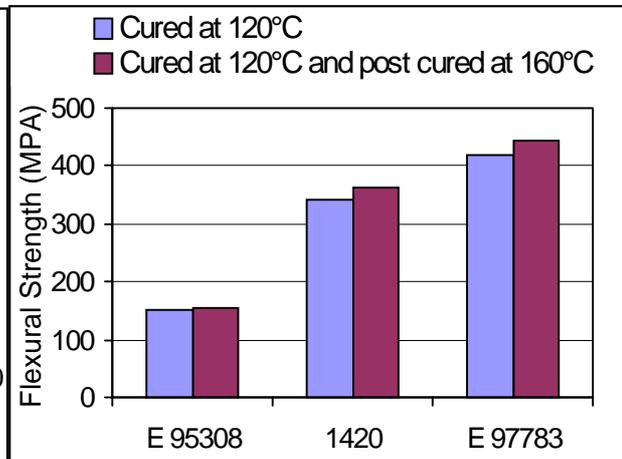


Fig. 8 The effect of Post-curing Treatment on Flexural Strength.

An increase in the fibre content of a Carbon Fibre Reinforced Phenolic Resin (applying resin 1420) from 40 to 48% results in substantial increase in flexural strength from 392MPa to 544MPa. This is not unexpected since reinforcing fibres constitute the principal load bearing components of the composites. Moreover, increase in the fibre contents of composites generally results in decrease in quantities of void entrapped in them [8]. Such a reduction in void contents is expected to also have a positive influence on strength. The comparative study of the three applied resins shows that the flexural strength of composite made from resin E97783 is highest followed by the ones made from resins 1420 and E97783 in that order (Fig.8). The free phenol and solid contents of the applied phenolic resin and the solvent used during resin preparation influence the flexural strength of the resulting composites. The poor strength of samples produced from resin E95308 is due to the poor wetting and adhesion between this resin and reinforcing carbon fibres and also to the negative impact of the many wide shrinkage cracks in the matrix of the composites on mechanical properties. The good wetting and adhesion between carbon fibres and resins 1420 and E97783 on the other hand enhance the mechanical properties of their composites. The good wetting property have more influence on strength than the high porosity in the matrix 1420.

Conclusions

With careful control of production process variables, good quality Carbon Fibre Reinforced Phenolic Resin Matrix Composites can be produced using simple gravity impregnation of carbon fibre preforms by liquid phenolic resins. The structure and properties of finished composites are markedly influenced by such characteristics of the applied resin as free phenol content, solid content and solvent used during resin preparation. For high strength, the optimum curing temperature is about 150°C. An increase in carbon contents by 8% of a typical composite from 40% results in over 38% increase in flexural strength. The thermal expansion behaviour of Carbon Fibre Reinforced Phenolic Resin Composite is influenced considerably by the orientation of the carbon fibre reinforcements.

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