INVESTIGATION OF THE STRENGTH AND FAILURE ENVELOPES OF NON-CRIMP GLASS FIBER REINFORCED THERMOPLASTIC COMPOSITES BASED ON IN-SITU POLYMERIZED CYCLIC OLIGOMERS

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Keywords: Thermoplastic, composite, cyclic oligomer

Abstract

This paper focuses on the fabrication and mechanical characterization of thermoplastic composites manufactured via hot compression method out of prepregs including non-crimp glass fiber reinforcements melt coated with cyclic butylene terephthalate (CBT). Both biaxial and uniaxial composite laminates were tested for mechanical performance. Strength parameters (X, X',Y, Y', S) of polymerized CBT (IPCBT) laminates were reported through the tensile and compressive testing of $(0°)_{12}$ and $(+45°/-45°)_{6s}$ laminates. Whereas the performance of biaxial laminates $(0°/90°)_{6s}$ were tested under tension, flexural and impact loading conditions for literature comparison. The ultimate strength comparison of unidirectional (UD) IPCBT laminates was evaluated through parallel testing of thermosetting vinyl ester (VE) matrix laminates.

1 Introduction

The question of manufacturing high quality thermoplastic composites parts still remain as an open problem because of inherent high melt viscosity of many of thermoplastic polymers which mostly causes poor fiber impregnation. The main limitation for processing however occurs in the case of structural continuous fiber reinforced composite manufacturing processes [1-5] where the high melt viscosity problem usually necessitates high pressure applications in order to have good fiber wetting and high fiber volume fractions which automatically adds expense [6]. As applied in liquid molding processes of thermoset resins this viscosity problem may be altered either using commingled yarns [7] or decreasing the polymer viscosity during impregnation [8]. Another approach that is specifically applicable for thermoplastic polymers, is the reactive processing of textile fiber-reinforced thermoplastics based on impregnation of the fibers with a low viscosity oligomeric precursor, followed by in situ polymerization [9]. CBT, as precursor, has been well studied for this manufacturing approach thanks to its low melt viscosity [10-13]. Throughout this method the pre-cursor impregnation is handled via conventional manufacturing techniques such as resin transfer moulding (RTM) [14] which is followed by an isothermal heating that leads to entropy driven ring opening polymerization resulting as linear high molecular weight matrix polymer.

Although thermoplastic composite materials may be manufactured with that approach, on an industrial scale they demand special designed equipment, time and equipment for resin/catalyst mix preparation and the most important thing is the narrow time window for impregnation (the time for the reactive mixture to reach 1 Pa s) which can allow to risks remaining dry places. Yet, it has also been shown that the pointed problems may be eliminated by using of properly prepared prepreg materials which also enables the manufacturing of complex shaped end products rather than laminates [15,16]. Following this motivation, the current study focuses on the manufacturing of non-crimp glass fiber reinforced polymerized CBT laminates (IPCBT) out of CBT/catalyst coated glass fabrics hot pressed at the polymerization temperature. Tensile, flexural and impact properties of the obtained biaxial $(0°/90°)_{6s}$ IPCBT laminates were determined. The efficiency of the new manufacturing method was sought via performance comparisons with reported literature values and effective microscopic investigation by scanning electron microscopy (SEM). Further investigation of newly initiated IPCBT laminates aiming the composite design integration was sought via determination of Tsai-Wu strength parameters (X, X', Y, Y', S) of UD $(0°)_{12}$ IPCBT laminates through tensile and compressive tests at longitudinal and transverse directions as well as tensile test of $(+45°/-45°)_{6s}$ laminates. Test results were compared with the results of simultaneously manufactured and tested VE laminates.

2 Experimental Procedure and Characterization

2.1. Materials

The prepregs containing non crimp glass fiber and CBT oligomer (CBT160 supplied by Cyclics Co. Ltd.) were manufactured and provided by Metyx Composites®. Number of butyl groups in the oligomer mixture varied from two to seven, thus having a melting temperature range between 130–160°C. CBT160 already contains a tin based compound as the polymerization catalyst. In the study, two kinds of reinforcement were used. L300 coded reinforcement, which has 300 g/m^2 areal weight, was used for the production of UD IPCBT laminates. L300 is stitched with synthetic yarn and consists of 600 tex glass fibre. For the production of biaxial IPCBT laminates, the reinforcement type was chosen as ±45° non crimp glass fiber with an areal density of 600g/m^2 including glass fibers with a mixing ratio of 50% of 600 tex, 50% of 300 tex of yarn number. Fiber mixing was preferred to eliminate the gap formation between fibers and to take advantage of different fiber diameters such as high tensile strength of 600 tex, high flexural strength of 300 tex due to the increased surface area. Initial fiber/resin weight ratio was set to 70/30 for all laminates. VE laminates were manufactured using L300 provided by Metyx Composites® embedded in Crystic VE-676-03 unsaturated vinyl ester resin supplied by Scott Bader Co. Ltd.

2.2. *Laminate Manufacturing*

Hot press molding process was used in the manufacturing of IPCBTs out of non-polymerized prepreg layers. Before hot pressing, the prepregs were dried overnight at 80˚C for the removal of residual moisture that may interfere with polymerization reaction. Hot press molding was carried out in a metal mould with 3 mm of thickness placed centre of the press. Substantial amount of preliminary work was done to determine optimum hot press parameters. At the final glance, the press temperature was set to 200˚C and the molding of laminates having sufficient number of layers were done under 1,6 MPa of pressure for 30 minutes. To avoid de-molding problems, the part was cooled to 180˚C prior to de-molding and was further cooled at room temperature. Flat composite plates in 250x250x3 mm dimensions with an overall fiber volume fraction of 54% were successfully manufactured. Correspondingly, VE laminates having 8 layers of UD reinforcement were manufactured via vacuum assisted resin transfer molding process. 2% cumyl hydroperoxide was mixed with the resin prior to

impregnation as curing agent. Vacuum bagging was done at the room temperature and under 0,9 bar pressure applied by means of vacuum pump. Cured parts were subjected to post curing at 80˚C for 3 hours. Overall fiber volume fraction of 52% was successfully achieved. All of the manufactured laminates were cut via water jet and divided into test specimens according to the test standard to be considered.

2.3 Mechanical Testing

Tensile test of IPCBT and VE composite specimens were performed as described in ASTM D3039 test standards. Test specimens were subjected to uniaxial tension with a constant displacement rate of 2mm/min and corresponding stress-strain values were recorded for maximum tensile strength and elastic modulus determination both in transverse and longitudinal directions with respect to fiber orientation. A micro-extensometer was used for displacement measurement. ASTM D695 test standard was considered for compression tests. Constant displacement rate was set to 1.3 mm/min. Compressive strength and modulus of the laminates were recorded. The impact resistance of the notched composite specimens was determined via Charpy impact tests done according to EN ISO 179-2 test standard. Flexural strength and modulus of the laminates were determined via 3-point bending tests done according to ASTM D790. At least five specimens were tested for each test case for the derivation of average test values.

2.4. Volume fraction and void content

Effective fiber volume fraction was measured via loss-on-ignition method. The samples were burned out in a furnace (Protherm PLF 115M) at 600°C for 2h. The void content of the samples was determined by carrying out density measurements according to ASTM D2734, followed by burn-out tests.

2.5. Cross Sectional Area Analysis

Scanning electron microscopy was used for the cross sectional area and surface characterization aiming to show the fiber wetting, compatibility of the resin and micro void formation. Sputter deposition of thin conductive gold coating was applied onto the sample surfaces. SEM micrographs were taken at various magnifications using a Philips XL 30SFEG Model electron microscope.

3. Results and Discussion

3.1 Analysis of Biaxial IPCBT composites

3.1.1 Cross Sectional Area and Surface Characterization

The wetting ability and impregnation quality were observed by SEM analysis. Figure 1 represents SEM micrograph of the peeled out surface of biaxial IPCBT laminate. Image confirms that there is a good interfacial bonding between the fiber and resin, IPCBT matrix strongly adhered to the fiber surfaces. The impregnation quality of IPCBT resin was further investigated by polishing the cross-section of biaxial IPCBT composites and by taking the SEM images. Figure 2a and Figure 2b with different zoom categories show that the composite laminate has well-impregnated area with only a few micro voids resulting in an overall void content of 3,7±0,9% according to burn out tests. Micro voids formation probably caused by the trapped air during the hot press moulding. However, any macro void which is possible to be formed between the glass bundles was not observed in the cross section of IPCBT composites. The results reveal that a good impregnation was achieved in the IPCBT-BANCGF composites in fact. Furthermore, the void content value obtained in this study is within the range of void content reported by other workers for noncrimp glass fabric composites. Parton [14] quoted void content value of 4,2±1,7% and large inter bundle voids

for UD IPCBT composites with 0,54 of V_f produced by RTM method. Another study by Vendramini et al. [7] reported a void content value as 3% for UD glass fiber reinforced PBT composites with 0,50 of V_f produced from commingled PBT/Glass fiber by hot compression at 240°C under pressure. When the SEM images and void content calculations were compared with the reported data of different production methods of PBT composites it can be said that the pre-impregnation of fibers with CBT named as prepreg can improve wetting ability and eliminate the big void formations.

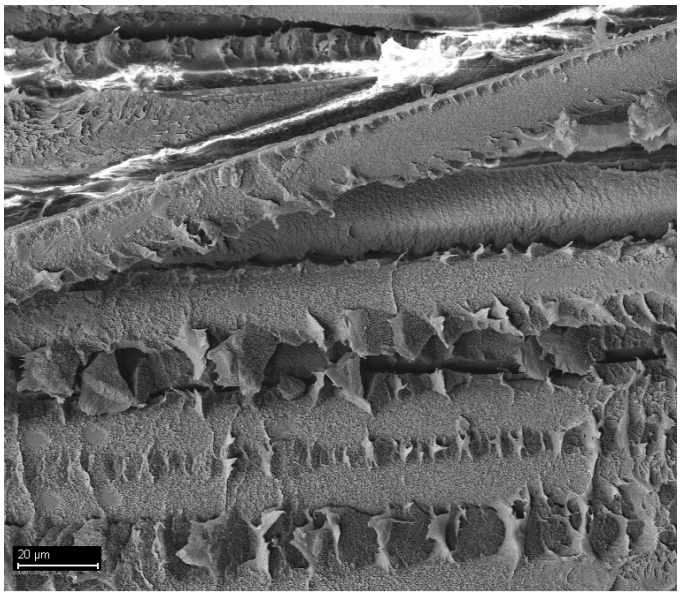
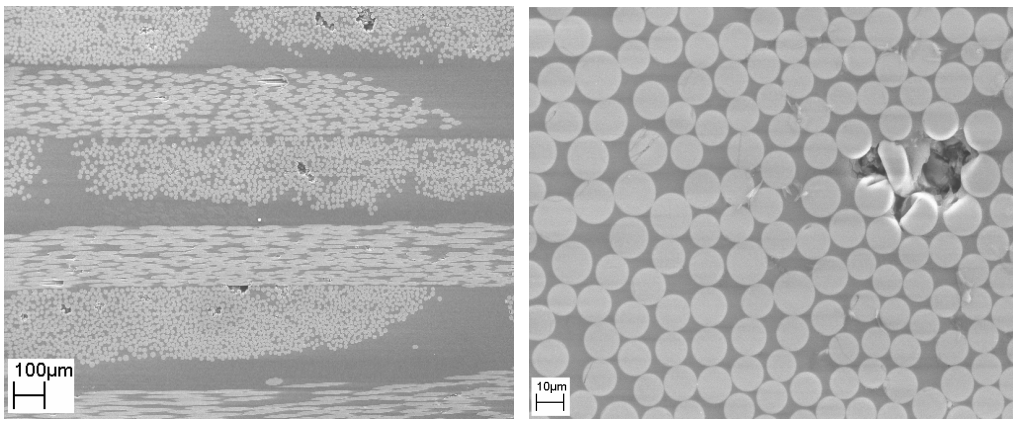


Figure 1. SEM image of the peeled surface of IPCBT composite laminate



(a) (b)

Figure 2. SEM images of cross sectional area of IPCBT composite laminate

3.1.2 Mechanical Test Results

The mechanical performance of biaxial IPCBTs was evaluated through tensile, flexural and impact tests. A brief summary of test results was given at Table 1. Since the manufacturing of IPCBT based laminates with different methods has already been discussed in the literature, an appropriate comparison was required. For instance, Parton[17], reported tensile strength and modulus values are 229±32 MPa and 19,8±0,7 GPa respectively for a biaxial reinforced (600 tex glass) IPCBT composite with a fiber volume fraction(v_f) 47 % produced by RTM. In the same study, tensile strength of 399± 7 MPa and tensile modulus of 18,0± 0,7 GPa were reported for woven reinforced PBT composite with 0,50 of Vf produced by compression

molding using commingled Glass /PBT hybrid fabric. On the other hand, Ishak et. al [12] reported that woven glass fiber reinforced IPCBT composites (v_f =0,54) manufactured by compression moulding had a tensile strength of 356 ± 9 MPa and tensile modulus of 20,6 ± 0,3 GPa dispersed CBT/Catalyst powder into the fibers during process. In the scope of this work the tensile strength of biaxial IPCBT laminates was found to be 482,4±8,3 and 21±1,3 respectively. Knowing that the tensile performance is strictly dependent on the reinforcement type, manufacturing quality and impregnation quality, we can at least say that the newly initiated IPCBT based laminates had a reasonable tensile performance.

Tensile Strength (MPa)	**Tensile Modulus (GPa)**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**	**Impact strength (kJ/m²)**
482,4±8,3	20,9±1,3	671,1±36,0	26,2±0,5	169,1±8,6

Table 1. Tensile and Flexural Properties of biaxial IPCBT composites

However, a remarkable difference in the flexural strength was observed for biaxial IPCBT laminates. As a simple comparison, the previously reported [17] biaxial glass reinforced (600tex) IPCBT laminates manufactured by RTM method had a flexural strength and modulus values of 343±60 MPa and 9,9±0,9 GPa respectively whereas the biaxial IPCBT laminates in this work had a flexural strength of 671 MPa ±36 and a flexural modulus of 26,2±0,5. It can be deducted that the obtained laminates were significantly stiffer. In the same study it was reported that the flexural strength and flexural modulus values are 283±26 MPa and 13,2±0,7 GPa respectively for woven glass fiber reinforced composite with 0,50 of V_f produced by compression moulding using commingled Glass /PBT hybrid fabric. Parallel to that Ishak et.al reported that IPCBT composite (Vf of 0,54) moulded by compression moulding using glass woven and dispersed CBT/Catalyst powder over the fabric during processing [12] has 578±8 MPa flexural strength and 24,5±0,3 GPa flexural modulus. The fracture mode of the biaxial IPCBT laminates under bending mode was dominated by interplay delamination and matrix cracking identified by sudden load drop at the end of testing. By considering the fact that both failure modes were governed by the matrix properties, one can conclude that the IPCBT matrix discussed throughout this study has a stiffer nature than the ones in the previously reported works. Also the improved strength can be attributed to better interlaminar damage resistance capability achieved by the pre-impregnation method.

The impact strength of the biaxial IPCBT laminates was determined to be 169,14±8,6 kJ/m² through notched Charpy impact testing. Since there exist no published work examining the impact performance of IPCBT based composite materials, the comparison was done with respect to its thermoset equal. Vinyl ester based composites having L300 (Section2.1) coded NCGF reinforcement with a lamination sequence of $(0/90)_{4s}$ was manufactured by vacuum infusion and tested subsequently. The notched Charpy impact strength of biaxial VE laminates were found to be 81,0±15,6 kj/m². This remarkable difference in the impact strength can be attributed to the inherent impact absorbing capability of thermoplastics with respect to thermoset based resins.

3.2. Analysis of Unidirectional IPCBT Composites

3.2.1 Mechanical Characterization

Table 2 summarizes the mechanical test results of UD IPCBT and UD VE laminates. Note that the fiber volume fraction for UD IPCBT laminates was 54% whereas it was 52% for UD VE laminates.

As an overall view, the reader may realize the clear performance superiority of UD VE-laminates which was pretty much an expected result when a thermosetting and a thermoplastic resin system is under comparison. However, it is vital to mention that the recyclability of UD IPCBT laminates is of crucial importance when making the one-to-one performance comparison.

Specimen Code	**Tensile Strength (MPa)**	**Tensile Modulus (GPa)**	**Compressive strength (MPa)**	**Compressive modulus (GPa)**
$(0)_{12}$ UD IPCBT	760,0±12,1	30,1±1,4	220,0±12,7	25,7±1,1
$(90)_{12}$ UD IPCBT	21,2± 1,1	7,8±0.3	61,9±4,5	7,1±3,7
$(+45/-45)_{6s}$ UD IPCBT	82,8±5,9	7,6±0,2	---	---
$(0)_8$ UD VE	916,5±16,2	44,9±1,1	300,0±22	25,4±1,2
$(90)_8$ UD VE	48,2±2,8	11,65±0,5	128,0±1,5	10,1±0,5
$(+45/-45)_{4s\ UD}$ UD VE	149,6±1,7	15,3±0.1	---	---

Table 2. Tensile and compressive properties of IPCBT and VE composites

The main problem that was predominantly effective in the fracture of IPCBT based laminates was the severe and early transverse matrix cracking. The main driving force in the occurrence of transverse matrix cracks may be attributed to the presence of uncontrolled residual stresses appeared during manufacturing process [18]. This behavior was initially identified from the testing of transverse tensile and compression tests where the matrix phase was carrying the majority of the applied load. Parallel to that, the significant strength difference under longitudinal tensile loading was related with the initiation of transverse matrix cracks from critically stressed (residual+applied) regions. At this point it is vital to underline that the occurring of matrix cracks may be repaired for thermoplastic materials. Hence this defect may be altered by re-processing. On the other hand longitudinal compression test results suggested a closer performance for both type of laminates. The fracture mode of UD VE laminates was initial plastic fiber kinking followed by the final fiber fracture at the edge of the kink band. Whereas the fracture of UD IPCBT laminates was either initiated by fiber kinking or followed by sudden delamination failure from the kinking crack tip or it was directly caused by delamination.

3.2.2 Failure Envelopes of UD Composites

Further performance analysis was sought through the creation of Tsai-Wu failure criterion based failure envelopes of laminates on σ_1-σ_2 and σ_2-σ_6 stress spaces. Failure envelopes were created by a simple progressive damage failure analysis done by MICMAC software offered by Stanford University. The progressive damage analysis enabled the creation of predictive points on the failure envelopes out of the anchor points provided by experimental results. In the scope of this analysis, Tsai-Wu failure criterion was taken as bases in the mechanical behaviour prediction of each laminate under different loading conditions. Figure 3a and 3b corresponds to the first ply failure envelopes of UD laminates where the competitive design space of IPCBT composite laminates was demonstrated in the shaded region.

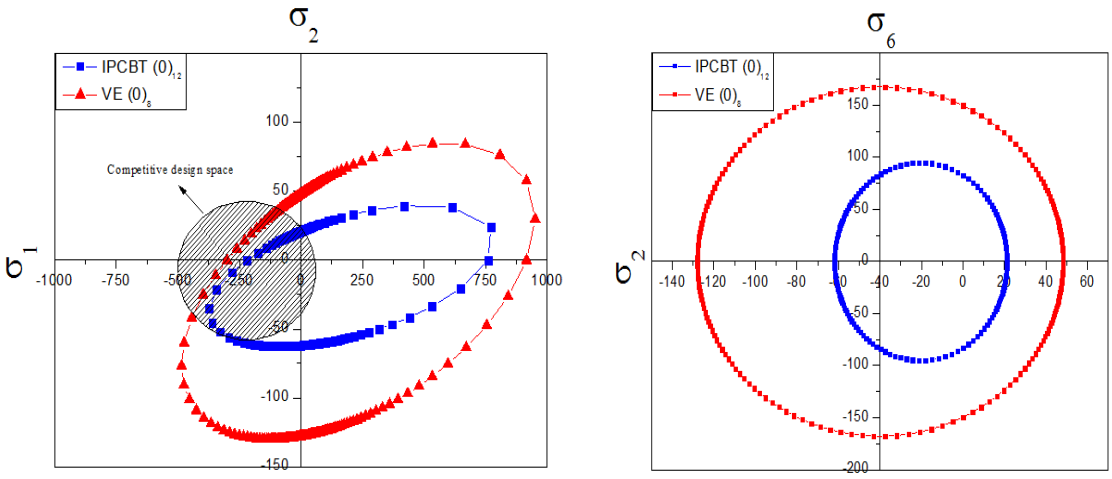


Figure 3. Failure Envelopes of IPCBT and VE based laminates in (a) σ_1-σ_2 and (b) σ_2-σ_6 stress spaces

Within this region of interest the mechanical performance difference of two laminates was minimum thus it can be said that it corresponds to the specific design space where it is safe to replace conventional VE based laminates with IPCBT based laminates. Contrary to that, the weakness of IPCBT based laminates under in plane shear loading may be seen from Figure 3b where the allowable design space of the laminates was remarkably different.

4. Conclusion

A new process was developed to produce non crimp glass fiber reinforced PBT matrix composites. Semi-isothermal processing of IPCBT composites via in-situ polymerization of CBT/Glass fiber prepregs has been successfully performed by means of hot press molding technique. Biaxial IPCBT composites gave better flexural and tensile properties when it was compared with reported results of IPCBT composites produced by RTM technique and the composites produced by compression molding of Glass/PBT commingled woven fabric in the literature. SEM analysis revealed that there is good interfacial bonding between IPCBT matrix and glass fiber. If more so, the micro void formation, probably caused by trapped air during compression, was reduced in respect of the composites produced by RTM. Thus, it can be concluded that the decreased distance between resin and fiber surface by pre-impregnation before compression process facilitates good penetration of the resin through inner fibers. Additionally, a detailed mechanical testing effort was done on the unidirectional laminates of IPCBT and was consecutively discussed with vinyl ester based laminates. Investigation of the test results and failure modes in accordance with the failure envelopes suggested that the IPCBT based laminates considered in this study can be strong alternatives to the VE based laminates especially under uniaxial compressive loading conditions as well as impact loadings. However, the performance of UD IPCBT laminates was found to be lower under tensile and in-plane shear modes due to high susceptibility to matrix crack formation.

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