INFLUENCE OF FIBER-MATRIX ADHESION ON MECHANICAL PROPERTIES OF GLASS/POLYBUTYLENE TEREPHTHALATE UNIDIRECTIONAL COMPOSITES

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Abstract

Interface failure plays an important role in determining the mechanical properties of polymer based fiber reinforced composite materials [1]. Results obtained from a study concerning the effect of matrix-fiber interfacial bonding on the transverse bending properties of glass fiber reinforced polybutylene terephthalate (G/PBT) unidirectional (UD) composites are presented in this paper. Six types of specimens were manufactured using three different processing methods, namely reaction-based resin, prepreg and commingled yarn systems. The transverse bending properties of the UD composites were measured. Furthermore, the tension failure zones after the transverse bending tests were examined using scanning electron microscopy (SEM) fractography analysis. Additionally, the quality of the composites was evaluated using complementary microscopic techniques (optical microscopy, OM and SEM).

1 Introduction

Te interface between the reinforcing fibers and the resin is a key factor in determining the mechanical properties of thermoplastic composites [1-2]. Microscopy has been widely used to examine the fracture surface of composites to pave light into the nature of bonding at the matrix-fiber interface and information relating material micro structure to mechanical properties [3-4]. Although the reinforcements mechanisms are similar, most of these studies were reported on epoxy based composites [5-6]. However, specific applications and complex structures require precise predictions of the mechanical behavior with respect to a particular fiber-matrix combination. The transverse bending test is widely used as a quick and reliable test method for the comparison and screening of different polymer composite systems [7]. In this work the transverse bending properties were measured, the fiber-matrix interfacial bonding of the fractured specimens were visualized using SEM, and the quality of the glass fiber reinforced polybutylene terephthalate (G/PBT) composites was evaluated.

2 Experimental procedure

2.1 Materials

Cyclic butylene terephthalate (CBT160) is in powder form at room temperature was supplied by Cyclics Corporation (USA). Glass fiber rovings supplied by PPG industries (USA) and Ahlstrom (Finland) were used with the CBT160 to produce a UD composites. Prepreg tapes were received from Ticona with 60wt% glass fibres, whereas prepreg tapes supplied by Jonam had 63wt% glass fibres, with a 0° orientation in both cases. Commingled G/PBT systems were supplied by Owens corning (France) and Comfil (Denmark). The G/PBT system delivered by Owens corning has copolyester Twintex, 65% GF by weight.

2.2 Processing of G/PBT Composites

The unidirectional G/PBT composites were manufactured using the vacuum consolidation

technique utilizing three different processing methods; commingled yarn, prepreg and reaction-based resin systems. The G/PBT systems were processed by *in-situ* polymerization of powdered CBT (for reaction-based CBT resin) and PBT for the prepreg and the commingled yarn. The recommended process temperature for CBT and PBT used are 230°C and 240°C, respectively.

2.3 Transverse Bending

The tests were conducted using a Zwick/Z100 testing machine operated in crosshead displacement control (3.3mm/min) at room temperature. During the testing, the load applied and the specimen deformations were recorded. The samples were loaded until the failure. Further the fractured area was examined using SEM microscopy. The fixture used was custom built to fulfill the requirements specified in the standard for the specific sample size. The test setup with dimensions is shown in Figure 1. The pins supporting and loading the test sample were not allowed to rotate freely during test. The G/PBT laminates were cut into rectangular samples, based on ISO 14125 class III standards, with dimensions 120 × 15 × 5 (mm^3). The thickness of the samples was measured using a vernier caliper. The specimen thicknesses were in the range 4.5 – 5 mm. The span, L, was adjusted to fit 100mm ± 0.2mm.

2.4 Microscopic Evaluations

The quality of the manufactured UD composites was evaluated (relatively) using several complementary microscopic methods on both the cross sections perpendicular to the fiber orientation of the polished specimens as well as the fractured surfaces. The microscopy gives information about voids, delaminations, fiber distributions and matrix rich areas. The following evaluation methods were chosen to compare the composite systems considered.

2.4. 1 Optical Microscopy (OM)

Reflected light micrographs of the polished Glass/PBT specimens were obtained using Olympus BX 60 (Denmark) connected to a Leica DFC320 camera. The Leica IM50 (UK) software was used to capture the images. For sample cross-sectional analysis, the specimens were grinded and polished with the following sequence of abrasive paper with grain sizes 500, 1200, and 4000 until a smooth surface was obtained. Samples were rinsed using de-ionized water during each step.

2.4. 2 Scanned Electron Microscopy (SEM)

The morphology of both polished cross sections and fractured surface (tensile tested) specimens were examined using Zeiss EVO 60 SEM with an electron source 10-25 keV in the secondary electron mode. To reduce the extent of sample arching, both polished cross sections and fractured specimens were coated with a thin layer of metallic gold in an automatic sputter coated prior to examination by SEM. The sputter coater uses argon gas.

3 Results and Discussion

3.1 Mechanical Properties - Transverse bending

A series of glass fiber (GF) reinforced PBT thermoplastic unidirectional (UD) composites with GF volume fractions of 41-52 wt. % were manufactured. The fiber content of the composites manufactured from commingled yarn was ca. 50 wt. % which allows the matrix to fully consolidate during vacuum consolidation. The fiber content for the prepreg systems was slightly lower, and varying fiber volume fractions were achieved for the case of reaction-based resin systems. Depending on the glass fiber sizing formulation assigned by the supplier and the composite processing conditions, the composites were expected to have slightly different fiber-matrix interfacial properties and thereby also different mechanical properties. Here, the correlation between transverse bending properties and composite quality factors governing the composite failure were investigated

The flexural strength and modulus of the G/PBT UD composites were measured. A summary of the test results are shown in Table 1. In most cases, the flexural modulus was higher for the composites with higher fiber volume fractions. For both commingled yarn and reaction-based resin systems higher flexural modulus values were observed. However there was no direct relationship between the flexural strength values and fiber volume fractions. Figure 2 shows typical (single data) stress-strain curves obtained from the flexural tests. It is observed that bot linear and non-linear composite responses were encountered. Specimen C1 exhibit a purely linear behavior, which is directly related to the brittle and

sudden failure observed. This type of failure behavior may generally due to the presence of non-wetted fibers (clear fibers) and therefore poor interface bonding. Specimen C2 exhibited non-linear behavior (ductile), which may due to good matrix-fiber bonding. For a few cases, the strain-stress curves exhibited discontinuous steps in the initial stages of stress-strain curves (linear portion). This phenomenon might be due to step-wise (discontinuous) damage process of the matrix and interface (debonding). Specimens, B2 and C2 with fiber volume fractions ca. 50 wt. %, showed better flexural properties.

3.2 Microscopic Observations

3.2.1 Cross-sectional analysis of polished G/PBT UD composites

Microscopy is widely used for the evaluation of nature of adhesion between the fiber and resin [3-6]. Both optical microscopy and SEM were used to analyze the distribution of fibers, the degree of wetting, occurrence of resin-rich areas and voids in the matrix. Figure 3 show optical micrographs (OM) of the cross sections of polished specimens; A1 to C2 and their corresponding higher resolution SEM micrographs are shown as inset figures. Micrographs of reaction-based resin specimens, A1 and A2 revealed large areas of resin-rich regions and only a few voids.

In specimen B1 arrangement of the fibers as bundles with uniform fiber wetting and packing were observed. Micrographs of specimens C2, C1 and B2 exhibited good fiber distribution. However, specimen C1 showed several non-wetted areas (clear fibers) and voids in the composites. In both commingled (C1 and C2) and reaction-based resin (A1 and A2) specimens, non-uniform fiber wetting and voids were observed in a few areas whereas the adjacent areas exhibited good fiber wetting which may due to the uneven consolidation process conditions of the composites.

3.2.2 SEM fractography observations - Post failure analysis

The material micro structure can be correlated qualitatively by assessing SEM micrographs of the fractured composite area [8]. Figure 4 show SEM micrographs of a fractured surface around a tension failure zone after a flexural test. The reaction-based resin specimens, A1 and A2 exhibited a significant amount of resin around the fiber surface (Figure 4 A1 and A2) and many hackles on the fiber surface (green arrows). However, debonding of fibers was observed in a few areas whereas no clear fibers were present in the fractured specimens. Several matrix cracks (brittle behavior) appeared along the resin-rich regions. In the failed specimen C1 clear fibers (yellow arrows) were present with or without resin residue and many debonded fibers were observed (Figure 4 C1). In specimens C2, B2 and B1, the individual glass fiber surface showed a thin layer of resin residue bonded to the fibers.

3.3 Influence of matrix-fiber interface bonding on the mechanical properties of G/PBT UD composites

The matrix-fiber interface bonding, fiber volume fraction and void content of a composite material to a large extent determines the stiffness and strength properties [1]. Thus, microscopic methods can be used to examine the matrix-fiber interfaces of the fractured specimen surfaces, and to correlate the observations with the mechanical properties of the composite. Table 2 summarizes the main evaluation criteria and the observed matrix-interfacial behavior in accordance with the SEM and OM micrographs captured for the the G/PBT composites. In summary, the prepreg specimens (B1 and B2) exhibited better quality with the lowest void content, whereas the commingled specimens (C1 and C2) showed good fiber distribution. Based on the microscopic evaluations, three types of failure modes were observed; namely matrix failure, interface failure and a mixed mode of failure.

The reaction-based resin specimens, A1 and A2 revealed a significant amount of resin residue and many hackles the around the fiber surface (Figure 4, green arrows) indicating a high level of adhesion. Accordingly a matrix dominant mode of failure was observed for these specimens in most cases. However in a few cases, fiber debonding was observed (Figure 4 B2, red arrow) which reveals a mixed mode of failure. Specimens A1 and A2 both exhibited cohesive failure at the resin-rich area [6]. The brittle failure observed at the resin-rich areas (Figure 4, A1 and A2) is in good agreement with the sudden failure events displayed in the stress-strain curves. Further, the discontinuous jumps that appeared in the stress-strain curves may be due to

the delamination or the initial failure of voids present in the composites.
It is well known that the void content of a composite may significantly affect its mechanical properties, and therefore it is an important indicator of the quality of a composite material. The micrographs of specimen C1 showed many non-wetted areas (red arrows) and clear fibers (yellow arrows), which may the reason for the sudden failure observed in the stress-strain curves. Thus the fracture occurs mainly at the interface (interfacial failure) as inferred from SEM the fractography micrograph (Figure 4, C1). It is well-known that the fiber dominated properties like tensile and bending stiffness and strength in the fiber direction are not very sensitive to matrix-fiber bond strength [1]. Here, a similar behavior was observed, as in the case of specimen, C1 where the test was performed in the fiber transverse direction. This supports their higher flexural modulus values for the fiber volume fraction of 51 wt. %.

Both prepreg specimens (B1 and B2) showed good fiber wetting with the lowest void content. The fractured areas of the specimen B1 showed fiber bundles surrounded by a resin rich phase as revealed in both the fractography, and the cross-sectional micrographs inferred a matrix failure mode. In specimens, B2 and C2 (Figures 4), the individual glass fiber surfaces showed a thin layer of resin residue. Further, the stress-strain curves (Figure 2) showed a linear behavior which could be due to high fiber volume fraction and uniform fiber distribution in these specimens. Both specimens exhibited a few hackles around the fiber and/or matrix areas and fiber debonded areas (Figures 4, B2 and C2) inferring a mixed mode of failure (matrix and interface failure). In summary, the SEM micrographs (Figure 4) indicates a matrix dominant mode of failure for specimens A1, A2 and B1; a mixed mode of failure for specimens B2 and C2, and finally an interface failure mode for specimen C1.

4 Summary and conclusions

The mechanical properties of G/PBT UD laminates were measured, and microscopy was used to to elucidate the correlation with the interfacial bond strength. The basic hypothesis being that the interfacial bond strength will be reflected directly by the measured transverse bending properties. In most cases, it was found that the specimens processed with higher fiber volume fractions follow this trend. However, the results obtained indicate that the matrix-fiber interfacial bond strength is not significantly affecting the mechanical properties of G/PBT UD composites. Thus, this study provides a better understanding of the relationships between processing, composite quality, fiber-matrix characteristics and the mechanical performance of composite materials.

Processing Method	Materials (G/PBT)	Fiber volume fraction, (V_f)	Flexural Modulus, E_f (GPa)	Flexural Strength, σ_u (MPa)
Reaction-based Resin (CBT 160)	A1	0.41	9.2 ± 1.3	49.8 ± 3.4
	A2	0.52	8.1 ± 1.1	45.3 ± 4.1
Prepreg Tapes	B1	0.46	5.9 ± 0.2	39.2 ± 3.5
	B2	0.49	7.8 ± 0.6	69.3 ± 5.1
Commingled Yarns	C1	0.51	8.4 ± 0.2	36.2 ± 2.5
	C2	0.50	7.1 ± 0.9	45.4 ± 1.8

Table 1. Summary of flexural test of G/PBT UD composites.

Processing Method	Materials (G/PBT)	Fiber volume fraction, (V_f)	SEM Observations		
			Clear Fibers	Hackles	Voids/non-wetted areas
Reaction-based Resin (CBT 160)	A1	0.41	No	Yes	A few
	A2	0.52	No	Yes	Yes
Prepreg Tapes	B1	0.46	No	Yes	No
	B2	0.49	No	Yes	Yes
Commingled Yarns	C1	0.51	Yes	No	Many
	C2	0.50	No	Yes	Yes

Table 2. Summary of SEM observations of interfacial morphology of G/PBT UD composites.

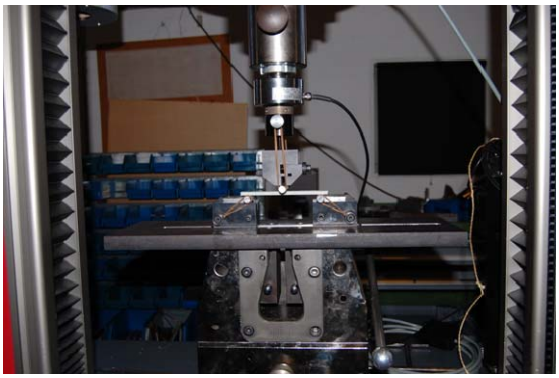

Figure 1. Dimension sketch of fixture used for performing the three-point transverse bending l = 120[mm], h = 5[mm], L = 100[mm], R1 = 5[mm] and R2 = 5[mm].

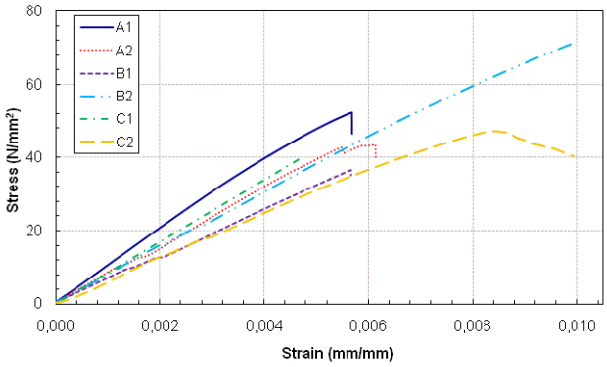

Figure 2. G/PBT specimens: Typical (single data) stress-strain plot from flexural test.

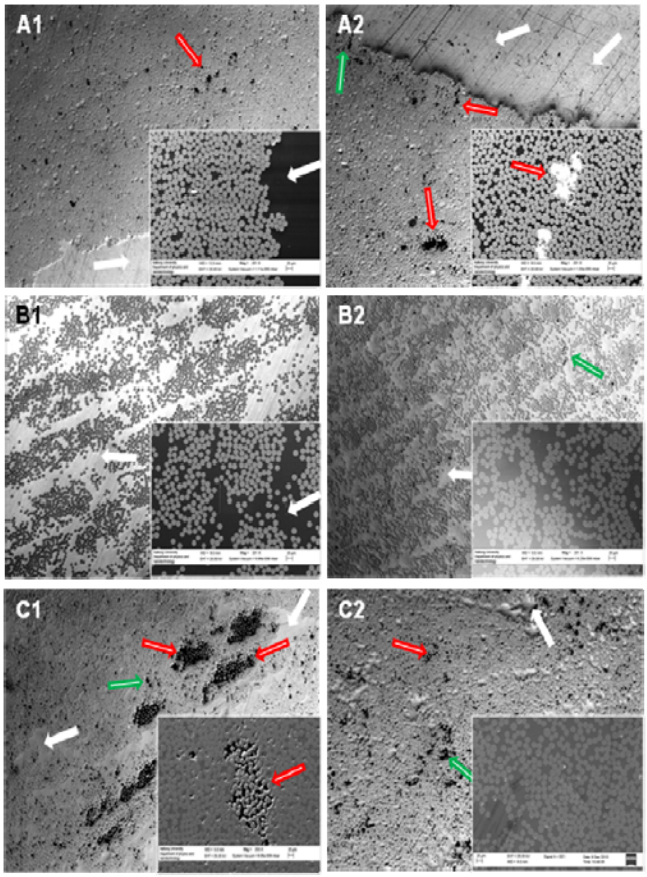

Figure 3. Optical micrographs of cross-sections of polished specimens, A1, A2, B1, B2, C1 and C3, respectively. Corresponding high resolution SEM micrographs are showed in inset.

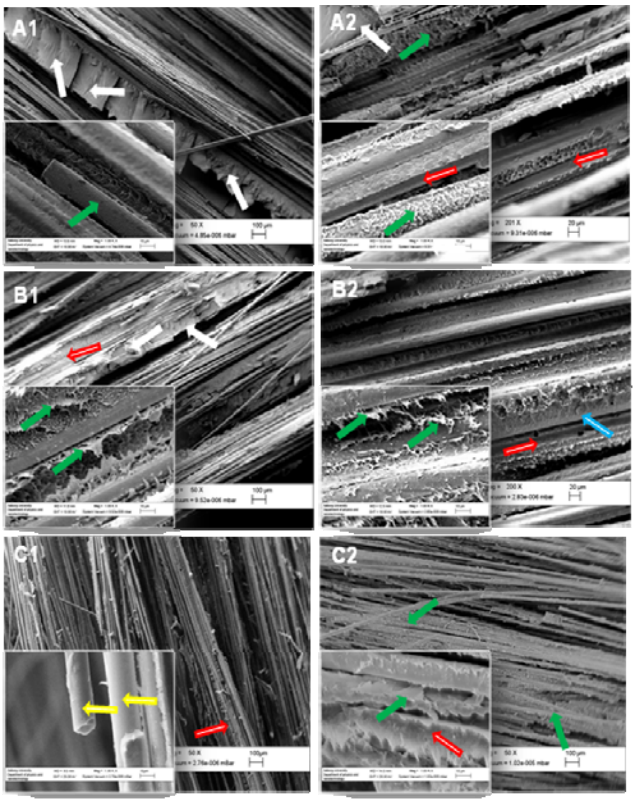

Figure 4. SEM fractography: Micrographs of fractured specimens, A1, A2, B1, B2, C1 and C3, respectively. Corresponding high resolution SEM micrographs are showed in inset.

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6 References

[1] M. R. Piggott, P. S. Chua, "Recent studies of the glass fiber-polymer interface", *Ind. Eng. Chem. Res.* 26, 672-677, 1987.

[2] Z. Fang and Q. Hu, "Influence of interfacial adhesion on strees-strain properties of highly filled polyethylene''. *Die Angewandte Makromolekulare Chemie*, 265, 4474, 1-4, 1999.

[3] K. Q. Han, Z. J. L and M. H. Y. Preparation and Mechanical Properties of Long Glass Fiber Reinforced PA6 "Composites Prepared by a Novel Process", *Macromol. Mater. Eng.* 290, 688-694, 2005.

[4] A. Warrier,A. Godara, O. Rochez, L. Mezzo, F. Luizi, L. Gorbatikh, S. V. Lamov, A. W. VanVuure, I. Verpoest, "The effect of adding carbon nanotubes to glass/epoxy composites in the fibre sizing and/or the matrix", *Composites: Part A* 41, 532-538, 2010.

[5] A. Voloshin and L. Arcan, "Failure of Glass-Epoxy Lamina - Fractographic Study", *Journal of Composite Materials*, 13, 240-246, 1979.

[6] V. Cecen, Y. Seki, M. Sarikant and I. H. Tavman, "FTIR and SEM analysis of polyester- and epoxy-based composites manufactured by VARTM process", *Journal of Applied Polymer Science*, 108, 2163-2170, 2008.

[7] ISO 14125; ASTM 790.

[8] D. Purslow, "Fractography of fibre-reinforced thermoplastics, Part 3. Tensile, compressive and flexural failures", *Composites*, 19, 358-366, 1988.