Graphite fabric reinforced PAEK composites by novel impregnation-co-film technique

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Keywords: impregnation-co-film stacking technique, poly(aryl ether ketone), graphite fabric, interface

Abstract
High performance polymers such as Poly(ether ketone) (PEEK), Poly(aryl ether ketone) (PAEK), Poly(ether ketone ketone) (PEKK), etc exhibit high melting points, 343 °C, 373 °C and 338 °C respectively and very high melt viscosity. They do not have appropriate solvents, which could open the ways to process their fabric reinforced composites; by impregnation technique followed by compression molding. Film stacking and powder sprinkling are the only possible techniques, which lead to weak crossover points due to non-wetting by the resin and finally resulting in inferior mechanical and interfacial properties and high amount of voids. In order to solve these problems, a novel technique called impregnation-co-film (ICF) is explored in this work. Polyetherimide (PEI) (10 wt% in dichloromethane solution) pre-impregnated graphite fabric prepregs were used before applying film technique followed by compression molding. The study compares properties such as density, void content, flexural strength, impact strength, Interlaminar shear strength (ILSS), thermal stability (in air) and interface by field emission scanning electron microscopy for the composite prepared with film stacking technique and that by impregnation-co-film stacking technique. It was confirmed that the new ICF technique proved to be significantly promising than the older technique almost in all aspects with 120% improvement in ILSS, 127% in flexural strength and 200% decrease in void content.

1. Introduction
Speciality polymers such as poly(ether ether ketone) (PEEK), poly(aryl ether ketone) (PAEK), Poly(ether ketone ketone) (PEKK) [1], thermoplastic poly(amide) (PI), poly(amide imide) (PAI), poly(ether imide) (PEI), poly (ether sulphone) (PES) [2, 3], are used as matrices to develop high performance composites. Apart from the type and amount of matrix, fibers (their types such as carbon, aramid, glass etc; their forms e.g. short, long, fabric etc; aspect ratio, adhesion with the matrix, orientation etc) and the type of processing technique also play an important role in controlling the performance of a composite [4–7]. It is a combination of matrix and reinforcement, which decided the selection of the processing technique.

Some polymers such as PEEK, PAEK, PEKK etc are extremely difficult matrices for developing fabric reinforced composites, since they do not have appropriate solvents, which would allow processing by easy and efficient impregnation technique. The only options left are film stacking or powder sprinkling. These suffer with serious problem of non-wetting at cross-over points of fibers by the matrix, leading to weaker spots, poor ILSS and overall having lesser performance than the estimated. There is hardly any solution to this problem barring usage of commingled fabric where the fabric is woven with fibers of matrix and reinforcement. During processing, polymeric fibers melt and wet the reinforcement. However, such composites finally become unidirectional (UD) rather than bidirectional (BD) [8]. Fujihara et al [9] studied the PEEK—carbon fiber micro-braided UD composite with better properties. PEEK–carbon fabric BD composites were developed by powder sprinkling technique by Sharma et al [10] and it was reported that the tribo-performance was not as per
expectation since fiber-matrix adhesion was minimal at cross-over points. Wang et al [11] used poly(aryl indole ketone) PAIK as a sizing agent (1–4 wt%) to modify the surface of carbon fabric to develop PEEK based composites, and reported that 1% PAIK based composite improved ILSS by ~62%. Hassan et al developed composites with PEKK sized carbon fabric (using 1 wt. solution of PEKK to size fabric), stacking it with PEEK films alternatively and reported improvement in ILSS, and flexural properties [12].

In the current work, impregnation-co-film (ICF) technique was employed to develop graphite fabric reinforced PAEK composites. Poly (ether imide) (PEI) was used as a matrix to reinforce fiber-matrix adhesion. The composite was characterised with various techniques, and the benefits due to new technique are described in the subsequent section

2. Experimental

2.1. Materials

Since, there is no solvent available for PAEK, film stacking method followed by compression molding was adopted to develop the composites. PAEK film (thickness and GSM of film were 50 μm and 65 gsm respectively) was procured from Gharda Chemicals Ltd Mumbai, India under the trade name of G-PAEK 1200F. Poly (ether imide) (PEI) (trade name ULTEM 1000, GE USA) was selected as interfacial matrix for graphite fabric. Graphite fabric (twill weave) was purchased under the trade name of SIGRATEX GDK 8045 from SGL Technologies GmbH, Germany. Solution of PEI in dichloromethane (10% by weight by vol.) in air tight container was used to impregnate the pieces (dimensions = 28 cm × 18 cm) of graphite fabric.

2.2. Composite development

Composites were developed in two stages. First stage involved impregnation of the graphite fabric in 10 wt% PEI solution for 3 h in a sealed container followed by drying. These prepregs were stacked with 6 pieces per fabric of PAEK film in an alternate manner and were placed in a mold. The mold was heated to 420 °C and pressure of 8 MPa was applied. Three breathing cycles were applied in order to remove the entrapped air/solvent/gases. Mold was then allowed to cool naturally. The composite was ejected using manual mechanism. Additional composite was developed without using strengthening of interface by PEI on fabric with a view to compare the influence of strengthened interface. These two composites were designated as C0 and C10. The PEI matrix pick up by the graphite fabric was observed around 28%. Table 1 indicates the composition for both the composites. PEI content in composites was calculated by considering difference in weight of piece of graphite fabric before and after impregnation. The PAEK and graphite fabric contents were calculated by thermo-gravimetric analysis.

2.3. Characterization of composites

2.3.1. Density measurement (ASTM D 792)

Density of the developed composite was measured using equation (1).

$$\rho_c = \frac{\rho_{\text{liquid}} \times W_{\text{air}}}{W_{\text{air}} - W_{\text{liquid}}}$$  (1)

Where $\rho_c$ is the density of composite, $\rho_{\text{liquid}}$ is the density of water used as a medium (1 g cc$^{-1}$), $W_{\text{air}}$ is the weight of a sample in air, $W_{\text{liquid}}$ is the weight of sample fully immersed in liquid.

Theoretical density of composite was calculated using rule of mixture, whereas void content was calculated using following equation (2) [13].

$$\text{Void content}(\%) = \frac{\rho_t - \rho_p}{\rho_t} \times 100$$  (2)

Where $\rho_p$ is the practical density, $\rho_t$ is the theoretical density

2.3.2. Thermogravimetric analysis (TGA)

Thermal stability of developed composites was studied in an air environment using Linseis 1000PT STA. Measurement range for the TGA was room temperature (RT) to 900 °C with ramp rate of 10 °C min$^{-1}$.
2.3.3. Interlaminar shear strength (ILSS) (ASTM D2344)
ILSS of composites were characterized as per ASTM D 2344 [14]. Width to length ratio of sample were maintained at 1:6 as per ASTM D 2344. Test samples were cut using diamond edge blade of Isomat precision saw. The test was repeated on five specimens to ensure the repeatability of results and average value was considered. Cross head speed was maintained at 1 mm min\(^{-1}\). The ILSS was characterized using Instron model 5982, Massachusetts, USA in three-point bending configuration.

2.3.4. Flexural properties of the composites (ASTM D790)
Composites were characterised for flexural strength (ASTM D790) [15]. This was evaluated on Instron model 5982, Massachusetts, USA in three point bending configuration, where span length, width and thickness were 64 mm, 12.7 mm and 3.5 mm respectively and loading speed was 2 mm min\(^{-1}\). The test was repeated on five specimens to ensure the repeatability of results and average value was considered.

2.3.5. Impact strength (ASTM D256)
The samples were cut using water jet cutter (OMEX USA) to avoid unnecessary kerf loss. Sample (length 64 mm, width 12.7 mm and centre notch of 3.2 mm depth and at angle of 45°) was tested on Izod impact tester (Model: IT 504 plastic impact, Tinius, Olsen, USA). at pendulum energy of 15.2 J. The test was repeated on five specimens to ensure the repeatability of results and average value was considered as per ASTM standard [16].

2.3.6. Vickers hardness (HV) for developed composites (ASTM E92-82)
Vickers hardness of composites were calculated using square-based pyramidal diamond indenter with face angle 136° using CETR UMT 3MT tribometer. Test was done with the help of ASTM E92-82 standard [17]. Indentation was done using polished cross section of a composite under the load of 40 N at five places and hardness was calculated using equation (3).

\[ HV = \frac{1.8544P}{d^2} \]  
(3)

Where HV is the Vickers hardness, P is the load (N) and d is the mean diagonal of impression (mm).

2.3.7. Interface analysis by field emission scanning electron microscopy (FESEM)
Interface of the composites was examined with the help of scanning electron microscope (FEI Quanta 200 F). 10 mm × 10 mm × 3.5 mm sized sample was cut with the help of diamond edge cutter (Isomat precision saw). Subsequently, thickness of sample was polished using 1000, 2000, 3000 and 4000 grade SiC paper (Make - JHON OKEY and 3 M) in order to achieve a smooth surface. The polished samples were gold coated and observed in FESEM.

3. Results and discussion

3.1. Physical properties
Figures 1(a) and (b) depicts practical density and void content of composites, indicating that the addition of PEI at the fiber-surface led to an improvement in the density by 9%, despite PEI being an amorphous polymer. Complementary to the density, void content in the C10 decreased by 190% compared to C0. High performance thermoplastic polymers such as PEEK, PAEK etc exhibit high melt viscosity, leading to inadequate flow of matrix around each strand of fabric causing high void content. In this case, addition of PEI solution with low viscosity at the interface proved that wetting of each filament in the fabric improved, leading to improvement in selected properties.

3.2. Thermo-gravimetric analysis (TGA)
Thermal stability is a significant property of composites, which plays a crucial role in tribological, structural applications and many more. Figure 1(c) shows thermal stability of composites with T\(_{5}\)/T\(_{on-set}\), whereas table 1 enlists T\(_{5}\)/T\(_{on-set}\) for all composites. C\(_{0}\) composite showed T\(_{5}\)/T\(_{on-set}\) of 551.65 °C followed by C\(_{10}\) at 533 °C. It can be clearly concluded that addition of PEI with thermal stability lower than PAEK led to reduced thermal stability compared to C\(_{0}\).

3.3. Hardness of the composites
Vickers micro-hardness (figure 1(d)) of C\(_{10}\) was higher than that of C\(_{0}\) by 300%, which was remarkable. It was mainly because of strong interface and continuity in the composite (matrix, interface and fibers) as seen in SEM micrographs as discussed in subsequent sections. In case of C\(_{0}\) higher void contents compared to C\(_{10}\) led to
relatively weaker microstructure and hence lower Vickers micro-hardness. The presence of amorphous and hard PEI matrix and its possible blending with PAEK leading to higher density and improved interface were also responsible for this significant improvement in Vickers micro-hardness of C10.

3.4. Mechanical strength of the composites

Figures 2(a)–(d) describes the Interlaminar Shear Strength (ILSS) (2a), Flexural strength and modulus (2b and 2c) and impact strength (2d). Following were the trends.

- ILSS- $C_{10} > C_0$ (121%)
- Flexural strength- $C_{10} > C_0$ (127%)
- Flexural modulus- $C_{10} > C_0$ (165%)
- Impact strength- $C_{10} > C_0$ (21%)

ILSS is direct quantification of fibre-matrix bonding in the composite [18, 19], and addition of PEI at the interface of fibers improved interfacial bonding possibly by forming high performance PAEK-PEI blend. Flexural strength and modulus showed improvement ($\approx 127$ and 165%) in $C_{10}$. It could be due to the addition of PEI during solution impregnation. It removed possible voids and wetted the fabric efficiently, including cross-over points, which was not possible in $C_0$.

It was not anticipated that the impact strength of $C_{10}$ would be higher than $C_0$ since $C_0$ contained more voids. It seems that inclusion of PEI has made the difference. PEI, an amorphous matrix, although in small amount (17 wt%), was able to absorb more energy and has surpassed the effect of voids and finally impact strength of $C_{10}$ was higher than that of $C_0$.

3.5. Interface analysis by scanning electron microscopy

Quality of the interfacial bonding for short fibre reinforced composites is widely reported with the help of fractographic studies [20, 21]. Since, the fabric reinforced composites have relatively higher fibre wt%, it is very difficult to perform...
A fractographic test on such samples. Hence, interface analysis was done on the specimens by polishing with fine SiC papers and then the samples were observed under FESEM. Figure 3 depicts the quality of interface with the help of FESEM micrographs. For C₀, Figure 3(a), shows that PAEK was unable to penetrate in the tows of fibers and hence the wetting of fabric was very poor, which led to lower density, greater void content and lesser mechanical properties. In the case of C₁₀ (Figure 3(b)), it showed better penetration of a matrix in the tows of fibers and had hardly any voids.

4. Conclusions

PAEK-graphite fabric composites developed with impregnation-co-film stacking technique using poly ether imide (PEI) solution for wetting the graphite fibers proved to be significantly effective for improving all...
properties (physical and mechanical) at the cost of slight deterioration in thermal stability by 18 °C. The density increased by 9% and void contents decreased by 190%. Mechanical properties of C10 proved superior to C0 as hardness increased by 300%; ILSS by 121%; flexural strength by 127%; flexural modulus by 165% and Impact strength by 21%. This was because of the stronger fiber-matrix interface due to inclusion of PEI matrix as confirmed from the FESEM microscopic studies.

Acknowledgments

Authors would like to acknowledge kind help from Mr. Rajesh Kumar and Dr. Kumud Arora Central Research Facility (CRF) IIT Delhi for FESEM characterization.

Data availability statement

The data that support the findings of this study are included within the article.

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