Fabrication and characterization of three-dimensional PMR polyimide composites reinforced with woven basalt fabric

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\textbf{A B S T R A C T}

A PMR polyimide composite reinforced with three-dimensional (3D) woven basalt fabric is fabricated for medium high temperature applications. The PMR polyimide matrix resin is derived from 4,4'-methyleneedianine (MDA), diethyl ester of 3,3',4,4'-oxydiphthalic (ODPE) and monoethyl ester of cis-5-norbornene-endo-2,3-dicarboxylic acid (NE). The rheological properties of the PMR polyimide matrix resin are investigated. Based on the curing reaction of the PMR type polyimide and the rheological properties, an optimum two-step fabrication method is proposed. The three dimensional fabric preforms are impregnated with the polyimide resin in a vacuum oven at 70 °C for 1 h followed by removing the solvent and pre-imidization. The composites are then consolidated by an optimized molding procedure. Scanning electron microscopy analysis shows that needle shaped voids are generated in yarns and the void volume fraction is 4.27%. The decomposition temperature and the temperature at 5% weight loss of the composite post-cured at 320 °C for 24 h are 440 °C and 577 °C, respectively. The dielectric constant and the dielectric loss of the composite are measured by circular cavity method at 7–12 GHz. The tensile strength and the modulus in the warp direction of the composite are 436 MPa and 22.7 GPa. The composite shows a layer-by-layer fracture mode in three-point bending test. The flexure strength and modulus in the warp direction of the composite are 673 MPa and 27.1 GPa, respectively.

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1. Introduction

Fiber-reinforced polymer composites are widely used in many engineering fields such as aerospace structures that require a high strength-to-weight ratio. Despite the use of unidirectional and two-dimensional (2D) polymer laminates over a long period, their use in many structural applications has been hindered by delamination [1], a long-standing problem with conventional polymer laminates reinforced with a unidirectional or 2D layered fiber structure [2,3]. Reinforcement of polymer composites with three-dimensional (3D) fiber architecture is an effective method to overcome the delamination problem [4–6]. 3D woven composites have excellent integrity and delamination resistance because there are three different types of yarns, namely as stuffer yarns, filler yarns and 2 yarns in the fabric construction [7,8]. In addition, 3D composites have improved fracture toughness, damage tolerance, resistance to impact, ballistic and blast loads. Many investigations have been carried out for investigating the mechanical properties and failure behavior of composites reinforced with 3D woven fabric [4–7,9–11]. Among the different technologies to produce 3D fiber architecture, 3D woven preforms have gained industrial acceptance [8,12–14]. Basalt fibers have a higher working temperature and better tensile strength and modulus than E-glass fiber as well as good resistance to chemical attack and thus have been used as reinforcement for composites [15–20]. Filament yarns of basalt fibers can be used for production of planar or 3D textile structures for composites [19]. The performance and cost of basalt fibers make them a potential alternative to glass fibers and carbon fibers. Dorigato and Pegoretti [21] prepared three kinds of fiber reinforced laminates with basalt, E-glass and carbon fabrics with the same areal density and found that the basalt laminates presented elastic moduli and strengths higher than those of their glass counterparts, with tensile strengths close to those of the carbon laminate. Basalt laminates...
also showed superior fatigue performances to those of the corresponding glass fiber composites. Quagliarini et al. [22] compared the tensile properties of basalt fiber reinforced polymer (BFRP) rods, glass fiber reinforced polymer (GFRP) rods, and carbon fiber reinforced polymer (CFRP) rods and found that compared with GFRP rods the tested BFRP rods seemed to be not so rigid but rather deformable with higher tensile strength. Therefore, they concluded that BFRP rods could be a good alternative to other fiber reinforced polymer rods. In this study, basalt fibers were used to weave the 3D woven preforms. Polyimide matrix is a kind of high performance polymer, due to its combination of excellent thermal–mechanical and thermal-oxidation properties as well as the good chemical resistance and dielectric properties [23–26]. PMR-15, one of the polymerization of monomer reactant (PMR) family polyimides, has relatively high temperature resistance and has been used as the matrix resins in fiber-reinforced composites for a variety of advanced aerospace applications [27]. PMR polyimides are generally capped at each end by a nadic endcap, which limits the average molecular weight of the oligomers and allows an improved processability. Although much research has been published on the processing and properties of fiber reinforced PMR polyimide composites or basalt fabric reinforced PMR polyimide composites. Chou et al. [29] presented the processing and properties of PMR polyimide composites reinforced with 3D multi-axial woven preforms.

In this study, a PMR polyimide composite reinforced with 3D woven basalt fabric was fabricated and the properties of the composite were investigated. By studying the rheological property and the Fourier transform infrared (FTIR) spectrum of the PMR polyimide matrix, a two-step impregnation/hot-compression method was established for the processing of PMR polyimide composite reinforced with 3D woven basalt fabrics. The thermal, dielectric and mechanical properties of the PMR polyimide composite reinforced with 3D woven basalt fabrics were investigated.

2. Experimental

2.1. Materials

The yarns used to weave the 3D preforms are basalt fiber filament yarns of 6144 dtex and type 3000, containing approximately 58.7% SiO₂ and 17.2% Al₂O₃, provided by Shenzhen Research Institute, Harbin Institute of Technology in China. The physical properties of the basalt fiber are presented in Table 1. One of the monomers, 4,4'-Methylenedianiline (MDA, Beihua Fine Chemicals Co., Beijing, China), was recrystallized in anhydrous ethanol for purification. The other monomer, 3,3',4,4'-Oxydiphthalic anhydride (ODPA, Shanghai Research Institute of Synthetic Resins, China), was used after baking in a vacuum oven at 180 °C for 6 h. Cis-5-norbornene-endo-2,3-dicarboxylic anhydride (NA, Nanxiang Chemical Reagents Co., Shanghai, China) was purified by vacuum sublimation. Anhydrous ethyl alcohol was dried by molecular sieves and freshly distilled prior to use.

Table 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Basalt fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear density (dTex)</td>
<td>6144</td>
</tr>
<tr>
<td>Tensile strength (GPa)</td>
<td>4.84</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>89.0</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.1</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.72</td>
</tr>
</tbody>
</table>

2.2. Weaving of 3D basalt fabric and preparation of monomer solution

The 3D woven fabric was manufactured with basalt filament tows. The schematic diagram of the fabric is shown in Fig. 1. The reinforcement geometry with four warp and five weft layers was adopted in making the composite preforms. The fabric counts in warp and weft directions were 5 ends/cm and 5 picks/cm while that of the z yarn was also 5 ends/cm. The surface of the basalt fabric and the cross-section of the corresponding composite are shown in Fig. 2. All the composite preforms were fabricated by a 3D weaving machine in our laboratory.

Three monomers, ODPA, MDA and NA, were used in the preparation of PMR type polyimide matrix resin. The monomer ODPA, which has a flexible ether bridge in the chemical structure, was substituted in place of 3,3',4,4'-benzophenonetetraacrylxylic dianhydride (BTDA) used in PMR-15 to improve the melt flow of the matrix resin. Diethyl ester of 3,3',4,4'-oxydiphthalic acid (ODPE) was synthesized by refluxing a suspension of ODPA in an amount of anhydrous ethyl alcohol calculated to yield a solution containing 40 wt% solid. The reflux was carried out for 2 h after the solid ODPA had been completely dissolved. Monoethyl ester of Cis-5-norbornene-endo-2, 3-dicarboxylic anhydride (NE) solution with solid content of 40% was prepared by refluxing a mixture of NA and ethyl alcohol by the similar method for ODPE preparation. The NE and ODPE solutions in ethyl alcohol were mixed with the solution of MDA in ethyl alcohol in a 1000 ml three-necked flask fitted with stirrer, N₂ inlet and gas outlet. The mixture was stirred for 8 h at room temperature to yield a homogeneous polyimide matrix resin solution with solid content of 40%. The molar ratio of NE:ODPE:MADA was 2:2.14:3.14, ensuring that the polyimide matrix resin had a calculated molecular weight of 1500.

2.3. Fabrication of 3D woven basalt fabric reinforced PMR polyimide composite

The polyimide matrix resin solution with solid content of 40 wt% was evaporated with a rotary evaporator at 45 °C to remove part of the solvent to yield a viscous solution with solid content of 65 wt%. The 3D woven preform reinforced PMR polyimide composite was fabricated by a two-step impregnation/hot-compression method. In the first step, 3D fabric preforms were impregnated with polyimide resin in a vacuum oven at 50 °C for 1 h followed by heating at 70 °C for 2 h to remove part of the residual solvent. The dry prepeg was then heated in a vacuum oven at 140 °C for
2 h, 190 °C for 2 h, successively. The processing procedure of the first stage was shown in Fig. 3. Amidization reaction and pre-imidization reaction occurred when the resin was subjected to the ramp and hold temperature scheme from 70 to 190 °C. Small molecules of ethyl alcohol and water released during the amidization and the pre-imidization reaction. In the second step, the composite was fabricated by hot-compression molding method according to the procedure in Fig. 4. The pre-imidized dry prepreg was placed into a stainless steel mold which was then placed in a hot press with a contact pressure. When the mold temperature reached 260 °C for 1 h, a pressure of 3–5 MPa was applied and the mold temperature was raised to 300 °C and kept for 3 h. After that, the mold was cooled and followed by pressure releasing. The fully-cured composite was obtained by postcuring at 320 °C for 24 h in a free state. The chemical and thermal process of PMR polyimide matrix resin was presented in Fig. 5.

2.4. Characterization

FTIR spectra of PMR polyimide resin thermally treated at different temperatures were obtained on a Nicolet 5700 Fourier transform spectrophotometer. Infrared samples were prepared as KBr pellets. Rheological measurements of the B-stage PMR polyimide matrix resin were performed on a TA ARES-RFS rotational rheometer. For micrographic investigation of the composite internal structures, cross sections of samples were polished using sandpaper and finally 0.1 μm OP-Alumina powder. Scanning electron microscopy (SEM) of cross sections were performed on a Jeol JSM-5600LV scanning electron microscope. Before the SEM observation, the cross sections were coated with a thin layer of gold to induce conductivity. Thermogravimetric analysis (TGA) was carried out with a NETZSCH TG209F1 thermal analysis system. The fundamental dielectric properties were measured at 5 frequencies (7.3, 8, 9.2, 10.5, 12 GHz) using an Agilent 8722ES Vector Network Analyzer by the circular cavity method.

Tensile tests were conducted on a universal testing machine, Instron 3382, and the crosshead speed was set at 5 mm/min. The samples were cut into 25.4 mm wide and 220 mm long using a diamond saw, with the length in the warp direction. Two stainless steel tabs of 1.0 mm thickness, 25.4 mm wide and 50.0 mm long were adhered to each end of a specimen using epoxy (Henkel Epoxy Extra Strong Glue) for better gripping and reducing stress concentration during the test. The gauge length of the specimen was 12 mm. A total of 12 specimens, 6 in each group, were prepared. An extensometer of 25.4 mm width was applied onto the specimen in the middle of the gauge length to transmit the extension during the initial elastic stage of the tensile test in order to exclude the compliance of the testing machine. The 3-point bending tests were performed on a universal tester WDW-20 (Jinan Hengshui Shengda Instrument Co, Shandong, China). Six specimens of 70 mm length and 15 mm width were prepared with a diamond saw. The diameter of the pins was 2 mm and the span between the support pins was 36 mm. The cross head speed was 10 mm/min.

3. Results and discussion

3.1. FTIR spectra of PMR polyimide resin

FTIR spectra of PMR polyimide samples at various stages of thermal treatment are shown in Fig. 6. Characteristic imide bands are present at 1780, 1380 and 735 cm⁻¹. Weak imide carbonyl absorption peak was present at low temperature and short treatment time (Fig. 3a), which caused by the fact that the monoethyl ester acid of 5-norbornene-2,3-dicarboxylic acid reacted with the amine very fast to yield the imide, even at room temperature [30]. As the thermal treatment proceeded and the sample was subjected to 140 °C for additional 2 h, the relative intensities of the imide bands at 1780 and 1380 cm⁻¹ increased (Fig. 3b). Further treatment for additional 2 h at 190 °C yielded a similar spectrum (Fig. 3c). The absorption in the range of 1550–1660 cm⁻¹ was assigned to the carbonyl stretching vibration of the amide and
carboxyl groups. The relative area of the imide absorption bands at 1780 and 1380 cm\(^{-1}\) increased with increasing temperature and time, while the amide absorption at 1550–1660 cm\(^{-1}\) decreased. The polyimide resin was partially imidized and the volatiles were released from the system with the baking temperature increasing from 70 to 190 °C. Retention of a small part of un-imidized segments in the polymer main chain could improve the molten fluidity of the resin in the thermal processing of the composites because of the un-imidized segment containing flexible substituents such as carboxyl and amide groups.

3.2. Rheological property of PMR polyimide resin

Rheological measurements were conducted on pre-imidized PMR polyimides with theoretical molecular weight of 1500 g/mol (M1500) and 2000 g/mol (M2000), which were subjected to the
ramp and hold temperature schemes depicted in Fig. 3. The rheological properties of M1500 and M2000 samples were measured under parallel plate flow mode with a heating rate of 3 °C/min from 200 to 320 °C (see Fig. 7). For the rheological curves of M1500 and M2000, an initial drop in viscosity during a temperature ramp from 200 to 260 °C and 200–270 °C, respectively. The viscosity of M1500 and M2000 decreased until the temperature reached 260 °C and 270 °C, respectively, because of the combination of pre-imidized polyimide softening and the isomerization reaction of the nadic endcap. When the temperature exceeded the critical transition temperatures, namely 260 °C for M1500 and 270 °C for M2000, the viscosity increased again due to the crosslinking reaction of the nadic endcap [31,32]. Similar tendencies in viscosity were observed for the rheological curves of the polyimide resin with different theoretical molecular weights. The melt-flowing behavior of the polyimide matrix resin is one of the important factors in fabrication of the composite. The temperature and the pressure applied in the hot-compression molding procedure should be carefully controlled. If the temperature was lower than the critical transition temperature, the polyimide matrix resin would not be sufficiently melted nor have good fluidity to impregnate the reinforcements effectively. Moreover, if the temperature was higher than the critical transition temperature, the rapid melting of polyimide matrix resin and crosslinking of reactive endcaps would occur simultaneously, resulting in a narrow processing window. In our study, the M1500 polyimide resin was chosen to fabricate the composite due to the lower melting temperature and lower melting viscosity. For M1500, critical transition temperature for optimizing the process cycle was identified as 260 °C. The optimum hot-compression procedure (shown in Fig. 4) was obtained from these properties.

3.3. Internal structure and voids volume fraction of the composite

Fig. 8 shows the cross sections of the composite samples. The z-binder yarns in the 3D orthogonal woven preform which originally had a quasi-square-wave profile experienced distortion induced by compression during the fabricating process, resulting in a quasi-sine-wave path as observed in Fig. 8a. In addition, Fig. 8 also showed small voids generated between fibers in yarns of the composite. Fibers and voids viewed in the warp yarn direction were shown in Fig. 8d, where the voids in yarns had irregular shapes and large aspect ratios. The needle shaped voids were possibly resulted from the difference in resisting forces against bubble growth in different directions as observed in previous studies [33]. Because of the constraint of the fiber in the direction perpendicular to the fibers, the resistance in the transverse to fiber axial direction was much greater than that in the fiber axial direction, and thus needle shaped voids were formed. In general, the mechanical properties of the laminated fiber reinforced composite would deteriorate significantly by a void content exceeding 2%. However, inclusion of voids in 3D woven fabric reinforced composite materials, owing to the reinforcement in the thickness direction, would not affect their properties as much as in unidirectional or 2D laminated composites [33]. The void volume fraction was calculated according to ASTM D2734 as follows:

\[
V_f = \frac{W_f \rho_f}{\rho_f}, \tag{1}
\]

\[
V_m = \frac{(1 - W_m) \rho_m}{\rho_m}, \tag{2}
\]

\[
V_v = 1 - V_f - V_m, \tag{3}
\]

where \(W\) is the weight fraction, \(\rho\) is the density, and the subscripts \(f\), \(m\), \(v\), and \(c\) refer to the fiber, matrix, void, and composite, respectively. Here, the density of the fiber and matrix were \(\rho_f = 2.73 \text{ g/cm}^3\) for basalt fiber and \(\rho_m = 1.31 \text{ g/cm}^3\) for bulk polyimide matrix; the \(\rho_c\) value is the apparent and bulk density of the composite and was obtained by ethanol immersion technique. Six specimens were used to calculate the volume fraction of void of the composite, and the average value of \(V_v\) was 4.27%.

3.4. Thermal property of the composite

Fig. 9 shows the TGA and DTG curves of the composite before and after postcuring at 320 °C for 24 h. Both specimen showed no
obvious weight loss before 400 °C, implying that the imidization was mostly completed. As the temperature was scanned to 850 °C, the samples before and after postcuring had weight losses of 13.2% and 12.5%, respectively. The onset decomposition temperature (Td) and the temperature at 5% of weight loss (Ts) for the composite after postcuring were 440 °C and 577 °C, respectively. For the composite before postcuring, the Td was 11 °C higher and Ts was 14 °C lower than those of the composite after postcuring. The lower Td of the composite after postcuring could perhaps be attributed to the degradation of the nadic endcaps. Upon further thermal treatment, the nadic endcaps cross-linked the double bond into a tough, heat resistant structure. However, the nadic endcap accounts for much of the weight loss when the cured PMR polyimide was exposed to high temperatures. Our results are much better than what has been reported in the literature [34,35]. Selladurai and coworkers reported that carbon fiber/modified PMR composites had the 10% weight loss temperature (T10%) of 455 °C, with the initial decomposition occurred somewhere beyond 400 °C [34]. The weight loss for their composite was 48% at 800 °C in nitrogen atmosphere.

3.5. Dielectric properties

The complex dielectric constant is expressed as \( e^* = e'_r - ie''_r \), where the real part \( e'_r \) and the imaginary \( e''_r \) are known as dielectric constant and dielectric loss, respectively. The dielectric constant and dielectric loss with respect to the frequency for the PMR polyimide composite reinforced with 3D woven basalt fabrics were presented in Fig. 10. It can be observed that the dielectric constant of the composite, which could be affected by the void content and the moisture content, was almost frequency independent. The dielectric loss was increased as the frequency increasing from 7 to 10.5 GHz and then decreased at 12 GHz. The dielectric loss showed a maximum value at 10.5 GHz which could be attributed to the dielectric relaxation or a resonance at that frequency. In our previous work, we found that for a 3D woven basalt/epoxy composite, the dielectric constant steadily increased with frequency while the dielectric loss drastically increased when frequency reached above 10 Hz [36]. That behavior was attributed to the frequency sensitive nature of basalt fiber. Obviously the PMR matrix in the basalt fiber composite played a significant role in stabilizing the dielectric properties of the composite as compared with epoxy resins.

3.6. Mechanical properties

A typical tensile stress–strain curve measured in warp direction for the composite is shown in Fig. 11. The stress increased linearly in the initial stage and then deviated from linearity as the strain exceeds 0.25% at which a significant non-linear response appeared which can be termed a “hardening phase”, that continued up to the failure at a strain of 2.88%. Cox et al. attributed the gradual stiffness reduction occurring in the hardening phase to “inelastic” straightening of the in-plane tows [37]. Different from the stress–strain curve of 3D woven carbon/epoxy composite observed by Cox et al., which showed a series of jagged peaks and small load drops due to the rupture of individual tows, the stress–strain curve shown in Fig. 11 increased smoothly and dropped suddenly as the composite ruptured completely at the peak tensile strength. When the strain exceeded 0.25% the composite gradually softened by around 20% until the strain reached to 0.5%. The gradual softening phenomenon is quite different from the sudden softening observed by Callus et al. in a series of 3D woven glass/vinyl ester resin composites [10]. In the range of strain from 0.5% to 1.2%, the stress–strain showed a quasi-linear path. Above a strain of 1.2%, the composite experienced continuous softening due to the widespread straightening of all the tows until the composite ruptured at the strain of 2.9%.

The elastic moduli in the elastic regime and hardening phase together with the tensile strength and failure strain of the composite measured in the warp direction were listed in Table 2. Mean tensile strength of the composite was calculated by dividing ultimate loads at rupture by their original area. Modulus in elastic regime and modulus in hardening phase list in Table 2 were determined from the initial linear region and the quasi-linear region in the strain range from 0.5% to 1.2% of the stress–strain curve, respectively.

Fig. 12 shows a typical load–displacement curve from the three-point bending test in the warp direction of the composite. In the three-point bending test, all the specimens broke at mid span where the central pin was located. It can be found that the specimens experienced a multi-state rupture rather than a catastrophic, sudden rupture at the ultimate load. Energy was released and stress wave emitted during crack growth. Since the crosshead moved at a constant speed, the deflection of the specimen from the peak load to the lowest level also represented the time duration for crack growth from zero to complete separation. Voids in the composite weakened bonding between fibers and matrix resin and might have provided initial cracks for the fracture. For the composite with relatively low voids volume fraction, the fibers were well bonded to the matrix and the load was transferred throughout the structure to all fibers. Cracks initiated in the bottom layer were able to propagate through the rest of the layers, resulting in a sudden rupture of the structure. While in the composite with relatively high voids volume fraction, as 4.27% in this
3D woven basalt preform reinforced PMR polyimide composite was successfully fabricated using an optimized two step impregnation/hot-compression method. The FTIR spectrum and rheological property of the polyimide resin were investigated for establishing an optimum manufacturing condition. For the PMR polyimide used in this study, critical transition temperature for applying pressure was identified as 260 °C, according to the result from the rheological test. SEM observation indicated that needle shaped voids were generated in yarns caused by the small molecule volatile releasing during the imidization and crosslinking. The volume fraction of voids was 4.27%. The results of TGA test indicated that the composite exhibited good thermal stability. The dielectric constant and dielectric loss of the composite were about 5.42 and 0.001 at 7–12 GHz, respectively. The decomposition temperature and 5% weight loss temperature for the composite postcuring at 320 °C for 24 h are 440 °C and 577 °C, respectively. Results of tensile test revealed that the tensile rupture process of the composite can be divided to two stages, the initial linear stage of elastic regime and the continued non-linear stage of hardening phase. In the hardening phase of tensile process, the composite experienced continuous softening until failure at a strain of 2.9%, perhaps due to the straightening of the tows. The modulus in elastic regime was 22.7 GPa and the modulus in hardening phase was 17.9 GPa calculated from the linear slope of the quasi-linear strain range of 0.5–1.2%. The tensile strength of the composite was 436 MPa together with a failure strain of 3.11%. The composite showed a layer-by-layer fracture behavior in the three-point bending test instead of a catastrophic failure mode. The mean strength and tangent modulus of the composite measured in the warp direction are 673 MPa and 27.1 GPa, respectively. It is concluded that the two step impregnation/hot-compression is an effective method for fabricating a 3D woven preform reinforced PMR polyimide composite.

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