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Process optimization of solvent based polybenzimidazole adhesive for aerospace applications

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ABSTRACT

The use of adhesive bonding for high temperature applications is becoming more challenging because of low thermal and mechanical properties of commercially available adhesives. However, the development of high performance polymers can overcome the problem of using adhesive bonding at high temperature. Polybenzimidazole (PBI) is one such recently emerged high performance polymer with excellent thermal and mechanical properties. It has a tensile strength of 160 MPa and a glass transition of 425 °C. Currently, PBI is available in solution form with only 26% concentration in Dimethyl-acetamide solvent. Due to high solvent contents, the process optimization required lot of efforts to form PBI adhesive bonded joints with considerable lap shear strength. Therefore, in present work, efforts are devoted to optimize the adhesive bonding process of PBI in order to make its application possible as an adhesive for high temperature applications. Bonding process was optimized using different curing time and temperatures. Epoxy based carbon fiber composite bonded joints were successfully formed with single lap shear strength of 21 Mpa. PBI adhesive bonded joints were also formed after performing the atmospheric pressure plasma treatment of composite substrate. Plasma treatment has further improved the lap shear strength of bonded joints from 21 MPa to 30 MPa. Atmospheric pressure plasma treatment has also changed the mode of failure of composite bonded joints.

1. Introduction

The use of polymer-based composite materials is becoming significantly popular due to their high strength to weight ratio, excellent corrosion resistance, outstanding thermal insulation and low thermal expansion. They have an impressive and diverse range of applications in automotive, aviation, spacecraft, civil infrastructure and sports industries [1–4]. Composite materials are often joined by adhesive bonding to form structural components. Though mechanical fastening is also being used for composite materials to some extent but adhesive bonding is given more preference over mechanical fastening because of some advantages. Adhesive bonding provides uniform stress distribution over the entire bond line while mechanical fastening creates large stress concentration around the drilled holes [5,6]. Also, adhesive bonding technique provides more design flexibility compared to the mechanical fastening [7–9].

With the development of high performance polymer based composite materials, high temperature adhesives are also required to form composite bonded joints. However, the use of adhesive bonding for high temperature applications is becoming more challenging. The main reason is that adhesive bonding has the limitation of being used at elevated temperature and under thermal cycling conditions. For some adhesives, oxidative degradation occurs at high temperatures whereas some adhesives show brittleness at low temperatures [10]. Epoxy adhesives are commonly used to bond epoxy based composites because of the compatibility between resin and adhesive. However, at elevated temperature, thermal and mechanical properties of these adhesives are degraded which ultimately degrade the performance of bonded joints. Consequently, these adhesives cannot be used at very high temperature [11,12]. Therefore, for high temperature applications, it is important to select an adhesive which can maintain its thermal and mechanical properties at high temperature.

Polybenzimidazole (PBI) is one such high performance polymer which has gained wide attraction in recent years. Polybenzimidazole (PBI) is a thermoplastic polymer which has the highest glass transition temperature (425 °C) of any commercial available organic polymer [13]. It has high decomposition temperatures (500–600 °C), good oxidation resistance and it maintains excellent strength at cryogenic temperatures [14]. Due to its high thermo-mechanical properties, it has great potential to be used as an adhesive for high temperature applications. In the past, PBI has been used as adhesive and was available in the form of film on glass cloth [15]. However, it required high processing temperature and pressure to form the bonded joints. Processing of PBI has been

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carried out by using a curing temperature of 370 °C with a pressure between 0.6 and 1.4 Mpa. Joints were postcured for 24 h each at 316 °C, 345 °C, 370 °C, and 400 °C followed by 8 h at 427 °C in air to achieve maximum properties. These were quite demanding conditions to form the bonded joints of PBI with high bond strength. Currently, PBI is also available in solution form with 26% concentration in solution. However, in solution form, PBI has not been tested as an adhesive. Due to high solvent contents, the process optimization required lot of efforts to form PBI bonded joints with considerable lap shear strength. Therefore, in present work, efforts are devoted to optimize the adhesive bonding process of PBI while using low processing temperature and pressure. This work only includes the process optimization followed by lap shear testing of PBI adhesive bonded joints at ambient conditions. Testing of PBI adhesive bonded joints at high temperature will be the scope of future work.

2. Experimental

2.1. Materials

26% concentrated solution of PBI in Dimethyl-acetamide (DMAc) was supplied by CELAZOLE, PBI performance products. DT120 epoxy based unidirectional (UD) carbon fiber prepreg was supplied by Delta Tech. In the following sections, the composite will be named as DT120/carbon composite. Composite laminate was prepared by stacking up the required number of pre-impregnated layers to achieve a cured laminate thickness of 4 mm. Laminate was prepared by curing the stacked layers in the autoclave at a pressure of 7 bars and at a temperature of 120 °C while using a heating rate of 5 °C/min. The laminate held at this temperature and pressure for 2 h and afterwards, it was cooled down to room temperature at the rate of 5 °C/min. At this point, the pressure was released and the laminate was removed from autoclave.

2.2. Thermal gravimetric analysis (TGA)

Thermal-gravimetric analysis (TGA) was conducted to determine the thermal stability of PBI adhesive using 60 μm thick film of PBI adhesive. PBI film was prepared using the same adhesive which was used for lap shear testing. The detail of film preparation is given in our previous work [16]. TGA experiment was performed using a Perkin Elmer Thermal Analysis Instrument (Pyris Diamond Thermogravimetric Analyzer). The sample was heated from a temperature of 25 °C to 550 °C at a heating rate of 10 °C/min. The furnace was purged with nitrogen gas to prevent oxidation at a flow rate of 25 ml/min.

2.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is performed using PBI film to determine the storage modulus and glass transition temperature of PBI adhesive. PBI film was prepared using the same adhesive which was used for lap shear testing. The detail of film preparation is given in our previous work [16]. The analysis was performed in tensile mode at an oscillation frequency of 1 Hz using the Perkin-Elmer dynamic mechanical analyzer (Pyris Dynamic Mechanical Analyzer). PBI film was cut in rectangular form having dimension of $(0.06 \times 8 \times 40)\ mm^3$ using a knife. Data is collected from 25 °C to 450 °C at a scanning rate of 3 °C/min.

2.4. Atmospheric pressure plasma treatment of composite specimen

Composite surfaces were treated with atmospheric pressure plasma using a TIGRES Plasma-BLASTER MEF equipment. The equipment operates at 230 V and 50/60 HZ frequency. Air was used as a gas for atmospheric pressure plasma treatment. Before performing the plasma treatment, the samples were first cleaned with methanol using an ultrasonic bath to remove any contamination on the surface. After cleaning, the specimens were dried in a vacuum oven at 80 °C for 4 h. Composite samples were plasma treated for 45 s prior to bonding.

2.5. Contact angle measurements

The change in the surface energy after plasma treatment was determined in term of contact angle value. A reduced value of contact angle indicates an improvement in surface energy of material which in turn improves the adhesion properties of materials. Contact angle measurements were carried out by the Modular CAM 200-Optical Contact Angle and Surface Tension Meter from KSV Instrument. KSV's CAM 200 is a fully computer controlled instrument based on video capturing of images followed by automatic image analysis for contact angle measurement.

2.6. Process optimization of composite bonded joints using PBI adhesive

PBI obtained from CELAZOLE contained high percentage of solvent. Therefore, it was very crucial to optimize the adhesive bonding process in such a way that desirable properties from PBI adhesive could be achieved. In this context, bonded joints of DT120/carbon composite were formed using PBI adhesive for bonding process optimization.

2.7. Specimen preparation for lap shear testing

Specimens for lap shear testing were cut to the dimensions of $(100 \times 25 \times 4)\ mm^3$ and they were adhesively bonded for single lap shear tensile tests. Five replicates were used during lap shear testing for each case. Prior to the preparation of an adhesive joint, degassing of the adhesive was carried out for 10 min in the vacuum oven at a pressure of 3×10^{-1} mbar while keeping the adhesive at room temperature. The purpose was to remove any air bubbles present in the adhesive. The lap shear tensile specimens were prepared by applying high temperature resistant PBI adhesive. Pressure was applied to the lap joint during the curing cycle by two standard clips. Bonded joints were formed using different curing temperatures for PBI adhesive in order to attain an optimum joint strength.

2.8. Scanning electron microscopy (SEM)

SEM analysis was performed to study the fractured surfaces in order to determine the failure modes after lap shear testing. Images were obtained using JOEL JSM-7500FE field emission scanning electron microscope (FE-SEM). Surface of each sample was gold sputtered to minimize sample charging effects.

3. Results and discussion

3.1. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was conducted to determine the thermal stability of PBI adhesive using a film of PBI. TGA curve of PBI film is shown in Fig. 1. PBI exhibited weight loss in two different temperature ranges. It has shown initial weight loss of 3.5% between a temperature range of 50 °C and 200 °C. The weight loss is more likely due to absorption of moisture by the polymer and any DMAc remained inside the polymer film.