NANO ADHESIVE BONDING OF HIGH PERFORMANCE POLYMER FOR AEROSPACE APPLICATIONS

S. Bhowmik[1], H. W. Bonin[1], V. T. Bui[1] and R. Benedictus[2]

[1]*Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario, K7K 7B4 Canada*

[2]*Faculty of Aerospace Engineering, Delft University of Technology Kluyverweg 1, 2629 HS Delft, The Netherlands*
Corresponding Author's Email: shantanubhowmik1@rediffmail.com

ABSTRACT: In this investigation, attempts are made to prepare nano adhesive bonding of high performance polymer such as Polybenzimidazole (PBI) (service temperature is –260 ^{0}C to +400 ^{0}C) for its essential applications to aerospace. In order to prepare high performance adhesive, nano adhesive is prepared by dispersing silicate nano particles into the ultra high temperature resistant epoxy adhesive (DURALCO 4703, the service temperature of the adhesive is –260 ^{0}C to +325 ^{0}C) at 10% weight ratio with the matrix adhesive followed by modification of the nano adhesive after curing under high-energy radiation for 6 hours in the pool of SLOWPOKE-2 nuclear reactor with a dose rate of 37 kGy/hr in order to essentially increase the crosslink density within the nano adhesive resulting in much improved cohesive properties of the adhesive. Prior to bonding, the surface of the Polybenzimidazole is ultrasonically cleaned by acetone followed by its modification under low-pressure plasma using nitrogen as process gas under RF glow discharge, in order to essentially increase the surface energy of the polymer leading to substantial improvement of its adhesion characteristics. First, the polymer surfaces are characterized by estimating surface energy and then the polymer surface is characterized by Electron Spectroscopy for Chemical Analysis (ESCA). The thermal characteristics of the basic ultra high temperature resistant epoxy adhesive and the high performance ultra high temperature resistant radiation crosslinked silicate nano adhesive are carried out by TGA and DSC and the physicochemical characteristics of these adhesives are carried out by the studies under solid state NMR. The TGA studies clearly shows that for the basic adhesive, there is a weight loss of the adhesive of about 10% when the adhesive is heated up to 325 ^{0}C resulting in deterioration of cohesive properties of the adhesive over the range of temperatures. However, in the case of the radiation crosslinked epoxy-silicate nano adhesive, there is a perfect 100% retention of weight of the adhesive when the adhesive is heated up to 325 ^{0}C resulting in significant improvement of cohesive properties of the adhesive over the range of temperatures. In order to determine the joint strength, tensile lap shear tests are performed according to ASTM D 5868-95 standard. Considerable increase in the joint strength is observed, more than 15 times when the polymer surface is modified prior to joining. Joints prepared with the unmodified polymer show only a joint strength of 1 MPa and increases up to 15.50 MPa with the surface modified polymer. There is a further massive increase in joint strength up to 25 MPa, when the joint is prepared by nano silicate epoxy adhesive and further modification of the adhesive joint under high-energy radiation results a further significant increase in joint strength up to 30 MPa. Therefore, with all the combinations there is about 30 times increase in joint strength. In order to simulate with aerospace climatic conditions, the joints are exposed to cryogenic (-80 ^{0}C) and elevated temperature (+300 ^{0}C) for 100 hours and further, thermal fatigue tests of the joints are carried out under 10 cycles by exposing the joint for 2 hours under the above temperatures. When the joint completely kept at ambient condition and the joint strength compared with those joints exposed to aerospace climatic conditions, it is observed that there is no difference in joint strength. Finally, to understand the behaviour of high performance silicate epoxy nano adhesive bonding, the fractured surfaces of the joints are examined by scanning electron microscope. It is observed that the joint essentially fails cohesively within the adhesive even when the joints are exposed to cryogenic, elevated temperature and thermal fatigue conditions. Therefore, this nano adhesive bonding of high performance polymer could be highly useful for structural application in future generation aerospace.

KEYWORDS: High Performance Polymer, High Temperature Resistant Adhesive, Silicate Nano Powder, High Energy Radiation, ESCA, TGA, Lap Shear Tensile Strength

INTRODUCTION

Reinforced polymer laminates especially; the polymers of high temperature resistance have many attributes that are highly desirable properties for applications in aerospace structures. Often in the fabrication processes, polymer sheets are joined by adhesive rather than by welding or riveting. The acceptance of adhesives as a high performance engineering material has grown steadily in the last few decades [1, 2]. Adhesives contribute highly to structural integrity, ease of manufacturing, enhanced performance, improved safety, and cost and time savings. Unfortunately, polymer surfaces are hydrophobic in nature and exhibit low surface energy and therefore, represent challenges for adhesive bonding. Hence, surface modification of polymers is often carried out to enhance their surface energy to overcome technological challenges [3].

However, the main problem with the application of polymer and adhesive for aerospace is high temperatures. This is caused by the aerodynamic friction heating of the structure as it moves through the air. Therefore, to solve the problems, it is necessary to use such high temperature resistant polymeric sheets such as polybenzimidazole (PBI) sheets, which also have excellent cryogenic properties (service temperature ranges from –260 ^{0}C to +480 ^{0}C). The PBI sheet can be joined with another PBI sheet by employing recently developed ultrahigh temperature resistant epoxy adhesive (DURALCO 4703, service temperature ranges from –260 ^{0}C to +350 ^{0}C) as this adhesive retains its cohesive properties even when exposed to cryogenic atmosphere.

In the recent times, research on polymer-clay nanocomposite has become a very important area because it is established that thermoechanical properties of polymer-silicate nanocomposite are far superior to those of conventional polymer or polymeric composites [4-*6*]. Therefore, with this principle, high performance adhesive can be prepared by dispersing silicate nano powder to matrix adhesive and that could open a new dimension on theromechanical properties of adhesive bonding.

In view of this observations, in the present investigation, the surface of polybenzimidazole sheet is modified by low-pressure plasma using a 13.56 MHz RF Glow Discharge for 120 seconds at 100 W of power using nitrogen as process gas, in order to essentially increase the surface energy of the polymer leading to substantial improvement of its adhesion characteristics. The PBI to PBI sheets are joined with an ultra high temperature resistant epoxy adhesive (DURALCO 4703, service temperature ranges from –260 ^{0}C to +325 ^{0}C) and by dispersing silicate nano powder into the ultra high temperature resistant epoxy adhesive at 10% weight ratio with the matrix adhesive followed by modification of the nano adhesive after curing under high-energy radiation for 6 hours in the pool of SLOWPOKE-2 nuclear reactor with a dose rate of 37 kGy/hr in order to essentially increase the crosslink density within the nano adhesive resulting in much improved thermomechanical properties of the adhesive. The low-pressure plasma exposed PBI surface is characterized by Electron Spectroscopy for Chemical Analysis (ESCA). The physicothermal characteristics of the basic ultra high temperature resistant epoxy adhesive and the high performance ultra high temperature resistant silicate nano adhesive is carried out by TGA. Tensile lap shear tests of the adhesive joints have been carried out to determine the effects of these environments on the joint strength. Finally, in order to understand the failure mode of the joints, the fractured surfaces of the joints after failure under tensile lap shear tests have been examined under scanning electron microscope.

EXPERIMENTAL

MATERIALS

In this investigation polybenzimidazole (PBI) sheets of service temperature ranging from –260 ^{0}C to +400 ^{0}C, tensile strength of 160 MPa and density of 1.3 gm/cc, were used for preparation of adhesive joint by using recently developed ultra high temperature resistant epoxy adhesive, DURALCO 4703, manufactured by Cotronics Corp. Brooklyn, NY, USA of service temperature ranging from –260 ^{0}C to +325 ^{0}C. The mixing ratio of resin to hardener, curing temperature and time of this adhesive are: 1:0.22, 25 ^{0}C and 24 hours, respectively. Silicate nanopowder of 50nm of particle size, manufactured by Glassven, La Victoria, Aragua 2121 United States was used as dispersing nano particles in 10% wt. ratio into the adhesive.

SURFACE MODIFICATION AND SURFACE CHARACTERIZATION OF PBI

Prior to joining, surface modification of the PBI is carried out by RF glow discharge using RF power generator that operates at a fixed frequency of 13.56 MHz. In this investigation, the surface of the polymer was modified under 120 seconds of exposure under 100 W of power. Surface characteristics of PBI are carried out by estimating surface energy of the polymer. Unmodified PBI and modified PBI surfaces are also characterized by ESCA.

PHYSICOTHERMAL CHARACTERIZATION OF ADHESIVE

Physicothermal characteristics of the basic ultra high temperature resistant epoxy adhesive and the silicate nano powder dispersed ultra high temperature resistant adhesive were carried out by TGA. TGA thermograms were obtained on a Universal V2 5H TA Instruments equipment, under a nitrogen atmosphere at a heating rate of 10 ^{0}C /min, and scanned from 25 ^{0}C to 500 ^{0}C.

PREPARATION OF THE ADHESIVE JOINT

The tensile lap shear test samples are prepared using PBI sheets of dimensions 125 × 25 × 6 mm^3 by applying the ultra high temperature epoxy adhesive at an overlap length of 25 mm. Any excess adhesive present at the interface was expelled out by pressing the joint under a load of 10 kg. The tensile lap shear test is performed according to the ASTM D 5868-95 standard, using an Instron Universal Testing Machine under a load cell of 10 kN at a test speed of 5 mm/min at room temperature. Three types of adhesive tensile lap joints were tested: (i) The basic ultra high temperature resistant epoxy adhesive lap joints of PBI-to-PBI,(ii) silicate nano powder with 10% wt. ratio was dispersed into the above epoxy adhesive and (iii) silicate nano powder with 10% wt. ratio was dispersed into the above epoxy adhesive and the joints were irradiated for 6 hours to SLOWPOKE-2 Nuclear Reactor with a dose rate of 37kGy/h. The schematic diagram of the reactor is shown in Fig. 1

DURABILITY TEST

From above three types of joints durability of the joints were carried out on the type (iii) specimens. The joints are exposed to cryogenic (-196 ^{0}C) and elevated temperature (+300 ^{0}C) for 100 hours and further, thermal fatigue tests of the joints are carried out under 10 cycles by exposing the joint for 2 hours under the above temperatures. For each set of environmental conditions, seven joints are tested and the mean value is reported in the result.

RESULTS

ESCA STUDIES ON THE PBI

ESCA wide scan spectra of the unexposed PBI shows the C 1s peak, O 1s peak and a significant concentration of F 1s peak as shown in Fig. 2. However, the PBI surfaces exposed to low-pressure plasma show significant decrease in F 1s peak, and a small increase in N 1s peak as shown in Fig. 3

SURFACE MODIFICATION OF POLYMER UNDER LOW-PRESSURE PLASMA AND WETTABILITY

When the PBI surface is modified by low pressure plasma, polar component of surface energy increases significantly, however, the dispersion component of surface energy remains almost same and therefore, due to the increase in the polar component in surface energy, a considerable increase in total surface energy of PBI is also observed as shown in Fig. 4.

TGA STUDIES ON BASIC ADHESIVE AND NANO ADHESIVE

The results from the TGA on physicothermal characteristics of the epoxy adhesive and the silicate nano epoxy adhesive are shown in Figs. 5 and 6 respectively. It is found that the degradation of the basic epoxy adhesive is a two-stage process: a relatively short stage with a very small percent of weight loss beginning at about 125 ^{0}C, followed by about 8% of weight loss up to 350 ^{0}C, attributed a degradation of the adhesive over the ranges of temperatures up to 350 ^{0}C and thereafter, there is a massive degradation of the adhesive. However, for the silicate-epoxy nano adhesive, degradation of the adhesive occurs in one stage as steady state continues up to 350 ^{0}C and there is no sign of degradation of the adhesive up to 350 ^{0}C. In this case, the percent of weight loss up to 350 ^{0}C is almost negligible as clearly evident from the Fig. 6.

LAP SHEAR TENSILE PROPERTIES OF THE PBI -PBI JOINT

Figure 7 shows the lap shear tensile properties of adhesive joints of PBI when the PBI surface has been modified by low pressure plasma. The figure reveals that the adhesive joint strength of the as received PBI to titanium is 1 MPa and increase to 13 MPa with the modification. It is observed that there is a considerable increase in joint strength up to 21 MPa, when the joint is prepared by nano silicate epoxy adhesive and further modification of the adhesive joint under high-energy radiation results a significant increase in joint strength up to 30 MPa as shown in Fig. 8.

DURABILITY OF THE JOINTS UNDER LOW TEMPERATURE, ELEVATED TEMPERATURE AND THERMAL FATIGUE CONDITIONS

It is observed that when the best joints i.e., the type (iii) joints are exposed to a low temperature (-196 ^{0}C) as well as an elevated temperature (+300 ^{0}C) for 100 hours, and thermal fatigue conditions with these temperature variations under 10 cycles by exposing the joint for 2 hours at each temperature the joints could retain almost 95 % of the joint strength as shown in Fig. 9.

DISCUSSION

This study examined high performance nano adhesive bonding of PBI to PBI, in the context of its structural applications for aerospace. Fig. 7 indicates that due to surface modification of PBI, adhesive joint strength is significantly high in comparison to the adhesive joint strength of as received PBI. This is possible because due to the increase in surface energy of PBI, essentially contributed to retaining the interfacial strength with the adhesive.

It is well documented by various researchers that thermophysical and thermomechanical properties such as melting, crystallization, thermal conductivity, coefficient of thermal expansion, tensile and breaking strength of epoxy as well as polyolefins improves considerably due to incorporation of silicate nano powder in to the matrix polymer [3-8]. The present investigation of nano adhesive bonding of PBI by dispersing silicate nano powder to ultra high temperature epoxy adhesive also shows a similar trend as there is a considerable improvement of thermophysical and thermomechanical properties of the adhesive. This is because in respect to any adhesive, the thermomechanical properties of silicate are significantly high and therefore, that essentially influence the overall performance of the adhesive.

An earlier investigation on influence of high-energy radiation on polymeric composite reveals that there is a considerable increase on the mechanical strength on the polymeric composite when exposed to high-energy radiation [7], because the exposure under high-energy radiation increases crosslink density within the polymer, essentially affecting the overall behaviour and mechanical properties of the polymer. Therefore, with the exposure under high-energy radiation, mechanical properties of the adhesive joint increase significantly because of increasing crosslink density within the adhesive [7, 8]. Therefore, in this investigation, the joints are essentially exposed to high-energy radiation so as to promote crosslinking within the adhesive by high-energy radiation, and as surface modified PBI to titanium adhesive joints essentially fail cohesively within the adhesive, so it is a clear justification to increase the joint strength up to 30 MPa with the nano adhesive bonding. However, when these PBI - PBI joints are exposed to climatic conditions such as elevated as well as cryogenic temperature related to aerospace and space conditions, the joints could retain the joint strength of about 95% of strength of the joint kept under ambient conditions. However, this could be within the acceptable limit in respect of aerospace applications.

CONCLUSIONS

The present investigation has led to the following conclusions:

(i) Polar component of surface energy leading to total surface energy of the polymer increases significantly due to surface modification of polymer by low pressure plasma

(ii) The adhesive joint strength of PBI to PBI increases considerably from 1 MPa to 13 MPa, when the PBI surface is modified by low pressure plasma.

(iii) There is a significant increase in joint strength up to 21 MPa, when the joint is prepared by nano silicate epoxy adhesive

(iv) When the joints are irradiated for 6 hours in the pool of SLOWPOKE-2 nuclear reactor, there is a further improvement of joint strength up to 30 MPa.

(v) When the joints are exposed to low as well as elevated temperature for 100 hours, and thermal fatigue conditions, the joints could retain about 95% of their the joint strength with respect to the strength of the joint tested under ambient condition.

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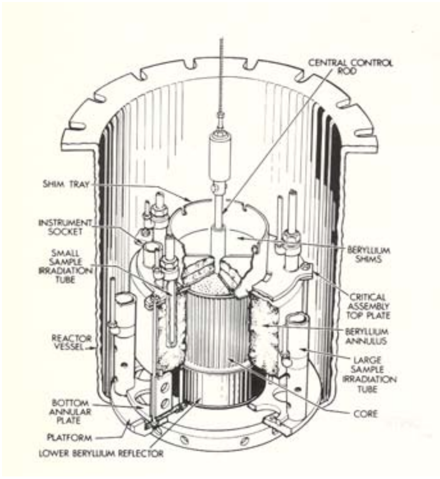

Fig 1. Schematic diagram of SLOWPOKE-2 nuclear reactor.

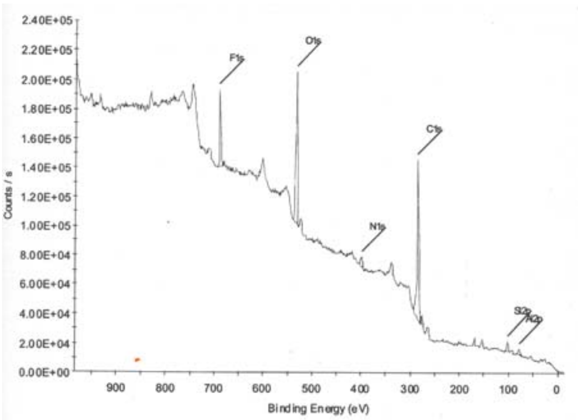

Fig 2. ESCA widescan spectra of unexposed polybenzimidazole surface.

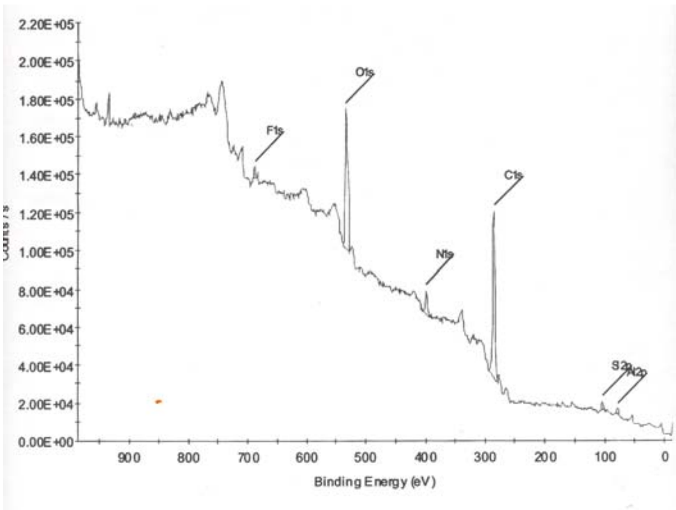

Fig 3. ESCA widescan spectra of polybenzimidazole surface modified by low pressure plasma.

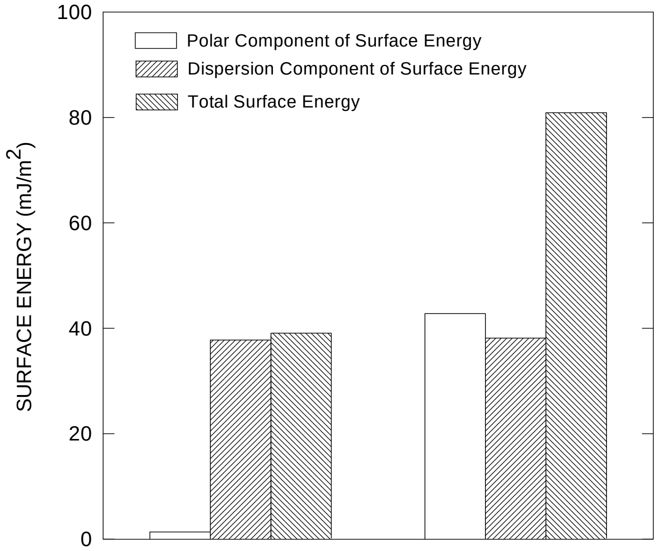

Figure 4. Polar, dispersion and total surface energy of polybenzimidazole when the polymer surface is modified by low-pressure plasma.

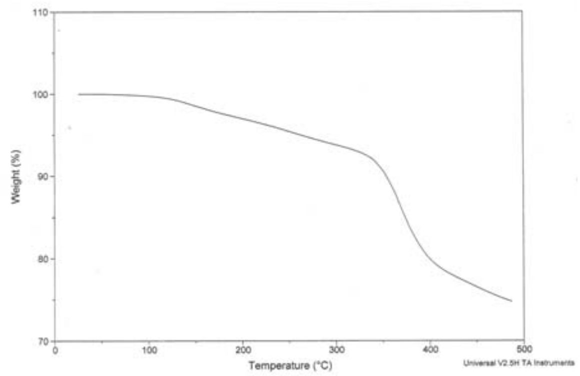

Fig 5. TGA plot of the basic high temperature resistance epoxy adhesive.

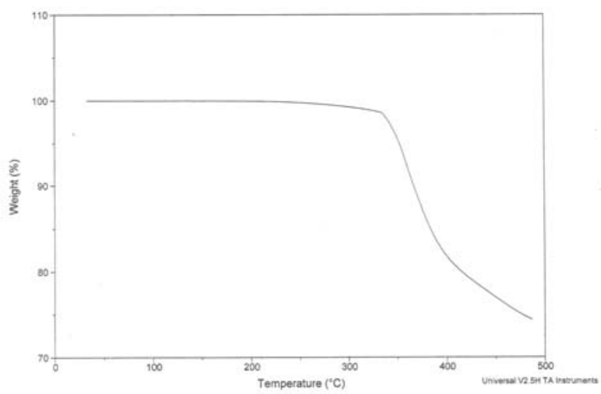

Fig 6. TGA plot of the high temperature resistant epoxy adhesive when silicate nano powder dispersed in to the adhesive in 10% weight ratio.

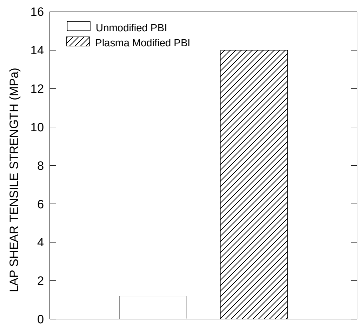

Fig 7. Lap shear tensile strength of adhesive joint of surface modified polybenzimidazole.

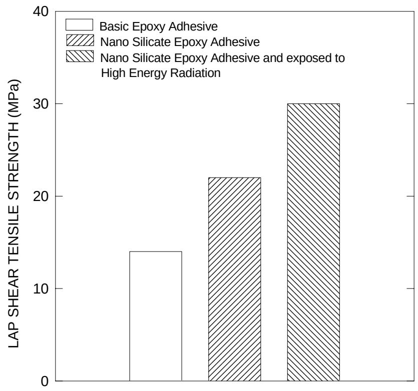

Fig 8. Lap shear tensile strength of the joint prepared with basic epoxy adhesive, nano silicate epoxy adhesive and the nano silicate epoxy adhesive joint exposed to SLOWPOKE-2 Nuclear Reactor for 6 hours.

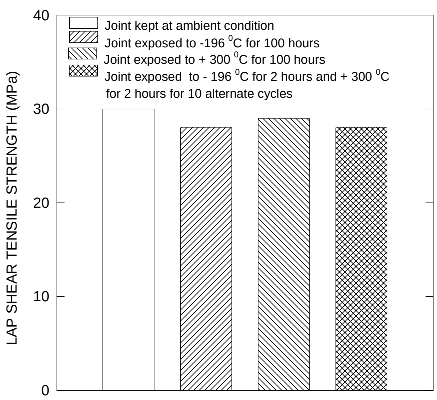

Fig 9. Durability under cryogenic, elevated temperature and thermal fatigue conditions of high performance nano silicate epoxy adhesive joint.