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Exploration of thermoplastic polyimide as high temperature adhesive and understanding the interfacial chemistry using XPS, ToF-SIMS and Raman spectroscopy

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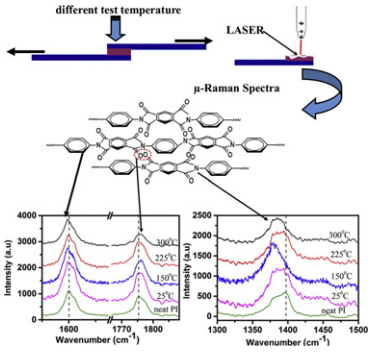
HIGHLIGHTS

- Polyimide showed good retention of adhesive strength at high temperatures.
- Raman spectroscopy (RS) has been utilized for detecting changes in polymeric structures as a result of stresses.
- XPS and ToF-SIMs helps in understanding locus of failure in relation to test temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermoplastic semi-crystalline polyimide (PI) was explored as an adhesive for elevated temperature applications for steel to steel joint. Its lap shear strength (LSS) at temperatures 25 °C, 150 °C, 225 °C and 300 °C was evaluated and analysed. The joints showed good LSS and remarkable retention up to 225 °C. The fracture mechanism was studied by scanning electron microscopy. Fractured surfaces at 25 °C and 150 °C showed shear elongated ductile type of failure features, while joint surface fractured at further elevated temperatures revealed weakened interface. The fractured surfaces were analysed using Micro-Raman spectroscopy (μRS), X ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToF-SIMS) to understand the failure mechanism of joint. μRS results showed changes in peak positions and intensity ratios of various functional groups as a function of test temperature.

1. Introduction

Aromatic polymers composed of aromatic rings linked to various functional groups are used for high performance applications [1–5]. In the area of high performance adhesives, recent years have witnessed an initiation of the use of some specialty polymers such as Polyimides (PIs) Cyanate esters, Poly(ether ether ketone) (PEEK) and Poly (aryl ether ketone) (PAEK) owing to their outstanding thermal stability along with very good mechanical properties and their retention to a fairly large extent at elevated temperatures. However, most of the commercial PIs are infusible and difficult to process and time consuming [6–8]. Interestingly a new class of semi- crystalline thermoplastic PIs has been recently commercialized, which are also melt processible [9]. Aurum PI (commercial name) is one of such high performance melt processible PIs, which exhibits very good mechanical and thermal properties [10]. Its feature of good retention of strength at higher temperature makes it a potential polymer for application as high temperature adhesives. However, no literature is available on its exploitation as adhesives.

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A lot of research has been done on investigating the changes in performance of adhesives on exposure to the aggressive environment in terms of temperature, humidity and/or corrosive media [11–13]. Since stress-strain properties of polymeric adhesives are highly dependent on the temperature, it is also important to consider the thermal effects because mostly, these lead to reduction in joint strength at higher temperatures, although opposite or mixed trends are also reported [14–16]. These phenomena necessitated the understanding of the interfacial properties. Interface between polymer and substrate plays a very important role in applications related to the adhesives, protective coatings and materials for resistance to wear and scratch. Interface is a region formed due to bonding reaction (physical or chemical) between the adhesive and substrate [2,17,18]. X-ray photoelectron spectroscopy (XPS) has proven to be an important tool in understanding the mechanism of adhesive bond failure. The chemisorption of organic compound on to the metal surfaces plays an important role in adhesion. Sugama et al. carried out XPS on the fractured surfaces of PAEK, poly (phenylene sulphide) (PPS), PEEK and polymer ether sulphone (PES) to analyze the polymer metal interface [19–22]. Time of flight secondary ion mass spectroscopy (ToF-SIMS) along with XPS have also been used to predict the exact failure mechanism in case of PEEK and epoxy based adhesives [12,23].

Raman spectroscopy (RS) has been utilized for detecting changes in polymeric structures as a result of stresses (thermal, tensile, or compressive) [24–26]. During high temperature lap-shear strength (LSS) test, the joint experiences significant shear stresses. These are temperature dependent and may lead to changes in various properties of polymers such as crystallinity, fragmentation of molecular chains and structure. An in depth analysis of variation in the polymeric structure during LSS test as a function of temperature has been rarely investigated by employing RS. The main objective of this study is to develop an understanding of molecular origin of stress induced vibrational frequency shifts and intensity changes.

These investigations were mainly intended to understand the failure mechanism in fractured joints of polymeric adhesives between metallic substrates at elevated test temperatures. Micro Raman spectroscopy (μRS), X-ray photo-electron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToF-SIMS) were explored for the same.

2. Experimental section

2.1. Materials

The thermoplastic semi-crystalline Polyimide (trade name AURUM PL450C) was supplied by Mitsui Chemicals Inc., Japan. The chemical structure is shown in Fig. 1, and mechanical and thermal properties are shown in Table 1.

Coupons of stainless steel (SS) (ASTM A 240-09a, Grade 316) with 0.1–0.15 μm roughness (R_a) were used as adherents. SS was selected as adherend because it has uniform thin layer of Cr_2O_3 and there is no variation from sample to sample. The surface with original roughness of the procured sheet was used since variation due to surface treatment was to be avoided.

Table 1
Physical and thermal properties of polyimide[a].

Property	PI
Density (g/cm^3)	1.33
Tensile strength (MPa) ASTM D638	92
Tensile elongation (%)	90
Tensile modulus (GPa)	2.76
Flexural strength (MPa) ASTM D790	137
Flexural modulus (GPa)	2.94
Glass transition temperature (T_g,°C)	250
Melting point (T_m, °C)	388
Melt flow rate (g/10 min) @ 400 °C and load 1.04 kg)	4.5–7.5

[a] Supplier's data.

2.2. Sample preparation

The SS adherends (LSS specimens) (15 mm × 65 mm × 1.5 mm) were degreased by acetone and dried before bonding. The LSS specimens were prepared using a specially prepared mold. While moulding temperature and pressure were 420 °C and 30 bars respectively and hold time was 20 min. The lap joints dimensions were controlled by using a specially prepared mold for developing lap joint with following dimensions overlap length 15 ± 0.5 mm, width 15 mm and joint thickness 0.2 ± 0.05 mm.

2.3. Dynamic mechanical analysis (DMA)

The viscoelastic behaviour was studied in tension by dynamic mechanical analysis (DMA + 150, MetraviB, France) with a frequency of 1 Hz. The displacement amplitude was 3.5 μm. Data were collected from ambient condition to 325 °C at a scanning rate of 3 °C min^{-1}. DMA specimens (3.8 mm × 10 mm × 13 mm) were cut from molded samples compressed at 420 °C and 30 bars with a hold time of 20 min.

2.4. Lap shear strength (LSS) test

LSS tests were carried out on INSTRON 5582, 100 kN load capacity UTM machine according to ASTM D1002 (with an integrated furnace capable of attaining 350 °C ± 5 °C). High temperature tests were carried out at 150 °C, 225 °C and 300 °C by keeping the sample in the furnace at the selected temperature for 20 min before application of load. The crosshead speed was kept at 1.3 mm/min. Five specimens were tested and the average of closest three readings was reported as the LSS value for that sample at that temperature.

2.5. Micro-Raman spectroscopy (μRS) analysis

To investigate the molecular deformation due to thermal and mechanical stresses, Renishaw inVia Raman spectrometer with 1064 nm wavelength diode laser was used. The sample was illuminated with a 1064 nm laser and on a 100×/0.85 NA objective with 830 l/mm grating.

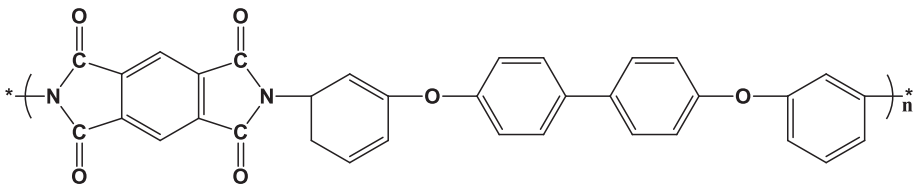

Fig. 1. Chemical structure of AURUM polyimide.