In this investigation, an attempt has been made to improve the interfacial adhesion characteristics of titanium (Ti) surface at elevated temperature and in aqueous salt solution. In order to ensure the presence of titanium oxide coating on the surface of titanium, anodization on titanium was carried out by sodium hydroxide. This oxide coating etches the surfaces of titanium. These etching surfaces of titanium increase the surface energy and surface roughness of the titanium. Physicochemical characteristics of surface modified titanium were carried out by X-ray photoelectron spectroscopy (XPS) study and the results reveal that there is a significant increase in oxygen functionalities due to anodization. The oxide etching on the surface of anodized titanium is further confirmed by scanning electron microscopy (SEM) study. The contact angle and surface energy are measured by the use of two liquids namely water and glycerol. It is observed that the formation of oxide not only improves the surface energy of titanium but also protects the surface of titanium when exposed to aggressive environments. The lap-shear tensile strengths of two anodized titanium surfaces were fabricated by adhesive. There has been significant improvement in the adhesive bond strength, and subsequently in the durability of adhesive bonded joint, of titanium when exposed to aggressive environments.

**Keywords:** Titanium alloy; sodium hydroxide anodization; XPS; AFM; adhesive bonding; tensile strength.
Comparative Studies of Solvent Bonding and Adhesive Bonding for Fabrication of Transparent Polymers

S. Ahmed, D. Chakrabarty, S. Bhowmik, and S. Mukherjee

Department of Polymer Science and Technology, University of Calcutta, 92, APC Road, Kolkata-700009
Department of Aerospace Engineering, Amrita University, Coimbatore 641112, Tamil Nadu, India
Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands
Facilitation Centre for Industrial Plasma Technologies, IPR, A 10-B, G.I.D.C, Sector 25, Gandhinagar-382044, India

Abstract—This investigation highlights rationale of solvent bonding and adhesive bonding for fabrication of a transparent polymer such as polycarbonate with a high-throughput process. Studies under ultra violet spectra and visible spectra reveal that in comparison with adhesive bonding of a polymer, solvent diffusion bonding is more transparent. Polycarbonate is hydrophilic in nature resulting in a low contact angle of water as well as the presence of polar functional groups on the polymer surface. It is observed that a lap shear tensile strength of a solvent bonding polymer is significantly higher than that of an acrylic adhesive bonded polycarbonate, and fabrication of polycarbonate by solvent bonding merely takes few seconds. Solvent bonding of a polymer results in a cohesive failure from polymer as analyzed under the scanning electron microscopy, this is why solvent bonding shows a significantly higher bond strength.

Keywords: adhesion, wetting, polycarbonate, solvent bonding, mechanical properties, industrial applications

DOI: 10.3103/S1068375516020022

1. INTRODUCTION

Amorphous-polymer-based microfluidic chips have generated significant interest in not only medical research due to some key advantages such as fast response time, low cost, easy disposal, excellent optical properties and suitability for mass production [1, 2]. Joining plastic composites in medical devices is becoming more complex and more sophisticated both in performance specifications and structural complexity [3, 4]. Most widely used methods for joining plastic in microfluidic devices are thermal bonding, adhesive bonding, and solvent bonding [5]. Chen et al [6] and Ogonczyk et al. [7] have emphasized that thermal bonding of a polymer at higher temperatures would result in the deformation and collapse of micro-channels. Micro-channels are most essential elements in microfluidic systems and, therefore, fabrication of polymeric channels is of great interest for biomedical application [8].

The ambient temperature bonding, such as adhesive bonding, is generally favored for fabrication of polymeric microfluidic devices [9], however, this method introduces another material to the interface, which can cause compatibility problems with the fluid flowing through micro-channels [10]. Recent articles published on solvent bonding in terms of fabrication of a polymer show that solvent bonding is a more effective method for joining a transparent polymer [11].

Moreover, this method results in aesthetic and homogenous joints with low weight and relatively strong bonding without introducing a foreign adhesive material [12]. However, selection of an appropriate solvent, optimization of various parameters of solvent bonding and durability of a solvent bonded transparent polymer under aggressive environment is yet to be established.

Based on these considerations, the objective of this work is to optimise performance of the solvent bonding of polycarbonate in comparison with the acrylic adhesive bonding of polycarbonate in respect of dimensional stability, manufacturing time, strength, and finally its durability under aggressive chemical environments.

1.1. Fundamental Aspects of Solvent Bonding

Thermodynamically, a polymer can be dissolved in a liquid spontaneously subject to the free energy of mixing, i.e., when \(\Delta G_{\text{mix}}\) is less than 0 [13]:

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}},
\]

where \(\Delta H_{\text{mix}}\) is the heat of mixing, \(T\) is the absolute temperature, and \(\Delta S_{\text{mix}}\) is the entropy change in the mixing process. Hence, an increase in the temperature affects lowering of free energy of mixing; thereby promoting dissolution. Therefore, for effective solvent
Epoxy–novolac interpenetrating network adhesive for bonding of plasma-nitrided titanium

S. Ahmed, D. Chakrabarty, S. Bhowmik, S. Mukherjee and R. Rane

1Department of Polymer Science and Technology, University of Calcutta, 92, APC Road, Kolkata 700009, India; 2Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, Delft, 2629 HS, The Netherlands; 3Department of Aerospace Engineering, Amrita University, Coimbatore 641112, Tamil Nadu, India; 4Facilitation Centre for Industrial Plasma Technologies, IPR, A 10-B, G.I.D.C, Sector 25, Gandhinagar 382044, India

(Received 2 December 2014; final version received 4 March 2015; accepted 5 March 2015)

This investigation highlights rationale to synthesize epoxy–novolac adhesive by novel interpenetrating network (IPN) technique. Physicochemical characteristics of the plain adhesive and IPN adhesive were carried out by Fourier transform infrared spectroscopy and thermal gravimetric analysis. Performing lap-shear test carried out plasma-nitrided titanium was fabricated with these adhesives and mechanical property of these adhesives. The blend of epoxy and novolac was optimized at 4:1 ratio, and the formation of IPN was confirmed by the suppression of creep with reference to neat epoxy and its swelling behavior. The adhesive with IPN shows significantly higher thermal stability than epoxy and leaves higher amount of residuals at the elevated temperature. Due to surface modification of titanium by plasma nitriding, wetting characteristics of titanium increases considerably and consequently, there was a significant increase in lap-shear strength adhesively of bonded titanium substrate.

Keywords: novel adhesive; titanium; plasma nitriding; lap-shear strength

1. Introduction

Adhesive bonding technology has shown itself to be capable of replacing conventional mechanical joining methods such as riveting,[1] welding, and mechanical fastening [2] in a variety of applications because of better fatigue performance and high strength to weight ratio.[3] Adhesive bonding shows structural integrity, ease of manufacturing, enhanced performance, improved safety, and cost and time saving.[4] In general, riveting and welding results in high stress concentration, which is absolutely negligible in the case of adhesive bonding where any stress developed, get distributed over the entire surface area,[5] and therefore, possibility of stress concentration is minimum.

It is to be noted that the main problem associated with the application of adhesive is its stability at elevated temperatures.[6] Novolac resins were commercialized long ago and have been widely used in industry till date due to their stable mechanical and thermal properties.[7] The mixing of polymers to get blend [through interpenetrating network (IPN) technique] considering novolac resin as one of the components, which is widely used for enhancement of physical and thermal properties,[8] Epoxy resins are characterized by its outstanding performances such as toughness, rigidity, chemical
Plasma nitriding on titanium surface for adhesion promotion

S. Ahmed¹, D. Chakrabarty¹, S. Bhowmik²,³*, S. Mukherjee⁴ and R. Rane⁴

This investigation highlights the influence of plasma nitriding on titanium surface in order to improve its interfacial adhesion strength with epoxy and epoxy nanocomposites adhesive. Surface energy of titanium increases considerably due to plasma nitriding implantation. X-ray photoelectron spectroscopy studies indicate the formation of various titanium nitrides, which are responsible for the increase in surface polarity. A reduction in equilibrium contact angle improves wetting on the surface and proper intimacy of the adhesive layer with two joining titanium surfaces. Thus, a greater surface area of contact with the adhesive layer helps uniform splitting of adhesive over the two titanium surfaces. A further improvement in bond strength is achieved on incorporation of 5% nanosilicate as reinforcement within the adhesive.

Keywords: Plasma, XPS, AFM, SEM, Tensile

This paper is part of a special issue on Diffusion

Introduction

Titanium alloy joints are widely used in aerospace industries demanding lightweight and reliability. It is used in aeroplanes, missiles and rockets where strength, low weight, resistance to high temperatures and corrosion resistance are of prime importance.¹,² For fabrication of titanium, at present, adhesive bonding is preferred. Adhesive bonding promotes structural integrity,³ ease of manufacturing,⁴ enhanced performance,⁵ improved safety⁶ and cost and time saving.⁷ Adhesive bonding is devoid of any stress concentration and, in case of any stress development, gets distributed over the entire surface area.⁸ Conventional adhesives like epoxy, polyurethane, etc. could not be used due to low thermal and mechanical properties of adhesive. Therefore, use of high temperature resistant epoxy with appropriately dispersed ceramic nanopowders in desired weight ratios is gaining significant interest and has been used to improve its thermomechanical properties.⁹,¹⁰ State-of-the-art review on this aspect reveals that proper surface modification is mandatory for promoting strong adhesion on titanium.¹¹ Surface roughening followed by plasma ion implantation has emerged a promising technology for the surface treatment of titanium.¹² Direct current plasma nitriding is a subatmospheric pressure process in which titanium sample is biased negative in a gas mixture, with nitrogen as the dominant gas.¹²

Based on these considerations, this study investigates state-of-the-art surface modification of titanium in order to improve adhesive bond strength of titanium. Profilometer and Vicker’s microhardness tester have measured surface roughness and hardness of titanium. Physico-chemical characteristics of unmodified and modified titanium surface have been measured by X-ray photo to analyse the changes on surface of the metal. The improvement in adhesion properties of titanium is correlated in terms of lap shear strength of the basic epoxy as well as epoxy nanocomposite adhesive joints on both native and plasma treated titanium surfaces. Finally, scanning electron microscopic analysis is used to investigate the failure modes of the adhesive bonded joints.

Experimental

Materials

In this investigation, titanium (Ti6Al4V alloy) sheets of grade 5 (ASTM B265) were used for this experiment. The high temperature resistant epoxy adhesive (DURALCO 4703) manufactured by Cotronics Corp. (Brooklyn, NY, USA) having the service temperature ranging from 225°C to 350°C was used for joining the titanium sheets. The mixing ratio of resin/hardener, curing temperature and time for this adhesive were 1:0.22, 120°C and 4 h respectively. Unmodified silicate nanopowder of 50 nm particle size, manufactured by Glassven (La Victoria, Aragua 2121 USA), was used as dispersing nanoparticles for reinforcement of adhesive. Two test liquids, deionised water and formamide of known polar (mN m⁻¹) and dispersion components (mN m⁻¹) of surface energy (mN m⁻¹) were used to determine the polar and dispersion components as well as surface energies (mN m⁻¹) of substrate materials.
Investigation on nanoadhesive bonding of plasma modified titanium for aerospace application

Sabbir Ahmed¹, Debabrata Chakrabarty¹, Subroto Mukherjee², Alphonsa Joseph², Ghanshyam Jhala² and Shantanu Bhowmik³

¹Department of Polymer Science and Technology, University of Calcutta, 92, APC Road, Kolkata-700009, India
²Facilitation Centre for Industrial Plasma Technologies, IPR, A 10-B, G.I.D.C, Sector 25, Gandhinagar-382044, India
³Department of Aerospace Engineering, Amrita University, Coimbatore 641112, Tamil Nadu, India
Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

(Received July 15, 2013, Revised September 18, 2013, Accepted September 20, 2013)

Abstract. Physico-chemical changes of the plasma modified titanium alloy [Ti-6Al-4V] surface were studied with respect to their crystallographic changes by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The plasma-treatment of surface was carried out to enhance adhesion of high performance nano reinforced epoxy adhesive, a phenomenon that was manifested in subsequent experimental results. The enhancement of adhesion as a consequence of improved spreading and wetting on metal surface was studied by contact angle (sessile drop method) and surface energy determination, which shows a distinct increase in polar component of surface energy. The synergism in bond strength was established by analyzing the lap-shear strength of titanium laminate. The extent of enhancement in thermal stability of the dispersed nanosilica particles reinforced epoxy adhesive was studied by Thermo Gravimetric Analysis (TGA), which shows an increase in onset of degradation and high amount of residuals at the high temperature range under study. The fractured surfaces of the joint were examined by Scanning electron microscope (SEM).

Keywords: titanium; plasma; adhesion; XRD; contact angle; SEM

1. Introduction

Titanium alloys are widely used in aerospace industries demanding lightweight and reliability. It is used in aeroplanes, missiles and rockets where strength, low weight, resistance to high temperatures and corrosion resistance are of prime importance (Bhowmik et al. 2009). According to Baker (2010), the normal approach to modify the surface properties of titanium alloy such as tribological characteristics is to increase the wettability and hardness of its surface with respect to the native one while retaining the bulk properties of the alloy intact. Recently, the AIRBUS Company is giving special attention for surface modification of titanium, which could enhance the adhesive bond durability (Bhowmik et al. 2006a).

*Corresponding author, Professor, E-mail: b_shantanu@cb.amrita.edu and s.bhowmik@tudelft.nl

Copyright © 2014 Techno-Press, Ltd.
http://www.techno-press.org/?journal=aas&subpage=7 ISSN: 2287-528X (Print), 2287-5271 (Online)