SURFACE MODIFICATION OF POLYIMIDE BY ATMOSPHERIC PRESSURE PLASMA FOR ADHESIVE BONDING WITH TITANIUM AND ITS APPLICATION TO AVIATION AND SPACE

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ABSTRACT

It is noted that in search of long term and efficient service performance in the context of future generation of aerospace materials, there is increasing need of metal-high performance polymer composite. Based on these considerations, high temperature resistant polymeric sheet such as Polyimide Meldin7001 sheet, is joined with Titanium sheet by employing ultra high temperature resistant Polyimide adhesive. In order to increase surface energy of Polyimide surface, atmospheric pressure plasma treatment is used to modify the Polyimide surface. Atmospheric pressure plasma treatment creates physical and chemical changes such as cross linking, formation of free radicals and oxygen functionalization in the form of polar groups on polymer surface resulting in improvement of wetting and adhesion characteristics. Surface of Polyimide (PI) sheet is treated with atmospheric pressure plasma for different exposure periods. Surface energy of PI sheet increases with increase in exposure time. However, after a certain exposure time of plasma, deterioration of surface layer of PI substrate results in degradation and embitterment of PI which is not suitable for adhesive bonding. Optical microscopic, SEM (EDS), analysis of treated and untreated specimen is carried out to examine the surface characteristics. Treated samples and untreated samples of Polyimide are bonded together with overlap joints. Lap shear bond strength of treated and untreated samples was measured by tensile test to study the effect of treatment on adhesive bond strength. The optimized time of plasma treatment suggested in this investigation results in maximum adhesive bond strength and consequently, this technology is highly acceptable for aviation and space applications.

1. INTRODUCTION

In recent times, considerable efforts are being made throughout the world to develop polymers and composite materials that are lighter in weight and have superior thermo-mechanical properties. These materials are often fabricated by adhesive bonding to form structural components. Adhesive bonding technique has shown itself capable of replacing conventional joining methods such as riveting, welding, and mechanical fastening in a variety of applications because of better fatigue performance and high strength to weight ratio [1, 2]. Mechanical methods cause stress concentration and reduce the overall load capacity of the structure [3]. An adhesive joint can distribute the applied load over the entire bonded area with more uniform stress distribution and is suitable for joining dissimilar materials with low manufacturing cost [3, 4]. The use of adhesive bonding for space application was restricted due to low thermal and mechanical properties of adhesives. However, due to the development of high performance adhesives the use of adhesive bonding technique in space industry has been increased rapidly in last few decades [5, 6].

In this context, recently developed ultrahigh temperature resistant Polyimide adhesive is used to study its thermal and mechanical properties. The service temperature for the Polyimide adhesive ranges from -50^{o}C to +375^{o}C, Polyimide adhesives have excellent resistance to most acids, alkalis, solvents, corrosive agents, radiation [7], making them extremely useful for aerospace and space applications.

Polymers have excellent physicochemical properties, and are easy to process. However, very often they do not possess the desired surface properties for adhesive bonding. They are hydrophobic in nature and in general exhibit insufficient adhesive bond strength due to relatively low surface energy [8]. For successful application of polymers to form structural parts using adhesive bonding, they need to have special surface properties like hydrophilicity and roughness [9]. Due to these reasons, surface preparation of polymeric adherends is the most important factor in the adhesive bonding process. The main purpose of surface preparation is to improve the adhesion properties to such an extent that adhesive failure does not take place.

A number of chemical and physical surface treatments have been developed for polymeric materials in recent years. Due to the disadvantage of chemical treatments, physical surface treatments are preferred to modify the surface of polymeric materials [10]. Plasma surface treatment is often the preferred way to treat the surfaces as it offers more stable and longer-lasting surface energy enhancement than any other treatments [11]. However, conventional plasma treatment also has shortcomings. It requires a low pressure (partial vacuum) and thus, the parts must be processed in a vacuum chamber, restricting the part size. Atmospheric-pressure plasma has been developed to operate at near ambient temperature and atmospheric pressure eliminating the expensive vacuum systems [10, 11].

Therefore, in the context of this study, atmospheric plasma treatment was employed to modify the polymer and composite surfaces. The surface energy of the specimens was estimated both for untreated and plasma treated specimens. Scanning electron microscopy was used to study the effect of atmospheric plasma treatment on the surface roughness of specimens. The improvement in adhesion properties of these materials after plasma treatment was correlated with lap shear strength of Polyimide adhesive joint. Lap shear testing was carried out for bonded joints of all types of polymers in order to determine the joint strength.

2. EXPERIMENTAL

2.1 Materials

In this study, High Temperature, Thermally Conductive Polyimide Adhesive 124-41, supplied by Creative Materials.Inc, Tyngsboro, MA. was used. The service temperature of this polyimide adhesive ranges from -55°C to +250°C and exhibits a Tensile shear strength of 18 MPa. The curing time for this adhesive is one hour at 175°C followed by subsequent post cure of five hours at 210°C. Before application of the adhesive to the substrate material, it was kept under vacuum for 20 minutes at room temperature to remove any air bubbles. Two test liquids, deionized water and formamide of known polar and dispersion components of surface energy were used to determine the polar and dispersion components of surface energies of substrate materials through measurement of contact angle by the sessile drop method. The known components of surface energy of liquids are shown in table 1.

Table 1.Polar, dispersion and total surface energy of test liquids

Liquids	γ_{LV}^{P} (mN/m)	γ_{LV}^{D} (mN/m)	γ_{LV} (mN/m)
Deionized Water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

Polyimide sheet MELDIN 7001 series supplied by Saint-Gobain Performance Plastics, Bristol USA was used in this study. This polyimide sheet has tensile strength of 72.5MPa at 22.5^{o}C and 38MPa at 260^{o}C.It has 8% elongation at room temperature. Polyimide sheets are highly thermal stable and also have good fire retardant so they are also widely used in high temperature applications.

Titanium Grade5 (TiA6V4) has many desirable properties like high strength to weight ratio, good corrosion resistance and high thermal stability. This make it infact most widely used titanium alloy in aerospace industry. On other hand this alloy has poor weldability, so mostly titanium sheets are joined together with adhesive rather than riveting or welding.

2.2 Thermal Characterization of Polyimide Adhesive

Thermo gravimetric analysis (TGA) was carried out to measure the decomposition and thermal stability of the Polyimide adhesive. Tests were performed using a Perkins Elmer Thermal Analysis Instrument (Pyris Diamond Thermogravimetric Analyzer). The samples were heated from room temperature to 600°C at a heating rate of 10°C/min. The furnace was purged with nitrogen gas to prevent oxidation. The flow rate of nitrogen was 25ml/min.

2.3 Plasma Treatment

To study the effect of plasma treatment, Polyimide sheet were treated with atmospheric pressure plasma. Samples were plasma treated using TIGRES Plasma-BLASTER MEF equipment. It operates at 230 V and 50/60 HZ frequency. For this particular study, the treatment distance of polymer surface from nozzle head of plasma equipment was 5 mm and the gas used for treatment was air with a total flow rate of 51 liters/min at a pressure of 4.5 bars. All the specimens were treated for 60 seconds. Before performing the plasma treatment, the samples were first cleaned in methanol using ultrasonic cleaning to remove any contamination on the surface. After cleaning, the specimens were heated under vacuum for four hours to dry. The specimens were then placed under the atmospheric pressure plasma and treated. In this investigation, the surface of the polymer was modified for intervals of 30, 60,120 and seconds. Where as titanium specimens washed with ethanol before joining with polyimide sheet to remove any loose contamination from surface.

2.4 Contact Angle Measurement and Surface Energy Estimation

The surface energy and its polar and dispersion components for Polyimide Meldin 7001 were calculated using contact angle measurement. Contact angles were measured by the sessile drop technique. Contact angle measurements were performed by the Modular “CAM 200– Optical contact angle and surface tension meter” using deionized water and formamide. The ultimate objective of measuring the contact angle was to estimate the surface energy of untreated and atmospheric plasma treated specimens. The surface energy and its polar and dispersion components for Polyimide were calculated using the following equation [12].

$$(1+\cos\theta)\gamma_{LV} = 2(\gamma_S^D \gamma_{LV}^D)^{1/2} + 2(\gamma_S^P \gamma_{LV}^P)^{1/2} \qquad [1]$$

In equation (1), θ is the measured contact angle of liquid with the solid surface, γ_{LV} is the total surface tension of the liquid, γ_{LV}^D is the dispersion component of the liquid and γ_{LV}^P is the polar component of the liquid. The total surface tension of the liquids 'γ_{LV}' and their polar 'γ_S^P' and dispersion 'γ_S^D' components were known. Contact angles of both liquids on the solid surfaces were determined by sessile drop method and then unknown dispersion and polar components of the solid surface were determined. Finally, the total surface energy 'γ_S' was estimated by adding γ_S^P and γ_S^D as given in Equation (2):

$$\gamma_S = \gamma_S^D + \gamma_S^P \qquad [2]$$

2.5 Adhesive Joint Preparation and Tensile Lap Shear Testing

Rectangular specimens, having dimensions 100x25x3 mm^3, were used for tensile lap shear testing. The specimens were bonded for single tensile lap shear tests. Prior to the preparation of an adhesive joint, degassing of the adhesive was carried out under a pressure of 1 Pa for 10 min. The tensile lap shear specimens were prepared by applying a high temperature resistant Polyimide adhesive. Any excessive adhesive present at the interface was expelled by mechanical pressing of the joint, which resulted in a joint having an adhesive thickness of about 0.20 mm. The adhesive thickness was controlled by adding 1 weight percent of glass beads in the adhesive and applying a uniform pressure on all the adhesive bonded joints. Pressure was applied to the lap joint during the curing cycle by two binder clips. The bonded specimens were cured at 175°C for 1 hour and subjected to subsequent post cure at 210^{o}C for five hours. Two types of Polyimide joints were prepared and tested.

- Untreated Polyimide and titanium joint
- Atmospheric plasma treated polyimide joint with titanium

Lap shear testing was carried out using a computer-controlled testing machine, ZWICK 2010, and a load cell of 50KN. The specimens were loaded in tension at a test speed of 5 mm/min. Five specimens were used for each material. All tests were performed at 22 ^{O}C and at 50% humidity.

2.6 Microscopic Studies of Substrate Surfaces and Fractrography

Scanning electron microscopy was used to study the surface roughness of the Polyimide sheet before and after atmospheric pressure plasma treatment. Also the study of fracture surface of the adhesive bonded joint after lap shear test was carried out. Images were obtained using a JOEL JSM-7500F field emission scanning electron microscope (FE-SEM).

3. RESULTS

3.1 Thermal Characterization of Polyimide Adhesive Using TGA

Thermo gravimetric Analysis (TGA) was performed to determine the thermal stability of polyimide adhesive as a function of temperature. A TGA scan for Polyimide adhesive is shown in Figure 1.This shows that the adhesive lost 20% of its weight up to 200oC.It is attributed to both evaporation of solvent present in polyimide adhesive and Curing of adhesive also start at this temperature. After 225oC the adhesive become stable up to a temperature of 390oC and only 4 percent of weight loss take place up to this point .From 400oC to 450oC there is a sharp decline of percentage weight and practically adhesive loss 25% of its weight and degradation of materials take place.

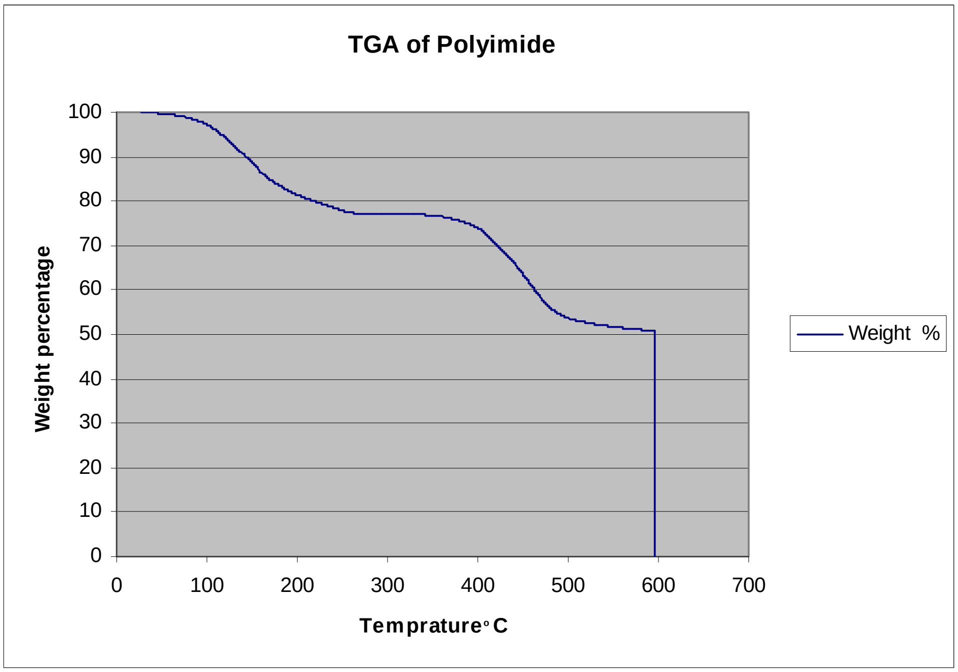

Fig 1. TGA analysis of High performance polyimide adhesive

3.2 Surface Energy of Modified Polyimide by Atmospheric Pressure Plasma

It is observed that due to surface modification of the polyimide by atmospheric pressure plasma, there is a significant increase in surface energy when compared to the surface energy of the untreated polyimide. A comparison of surface energy, its polar and dispersive components, for Polyimide before and after plasma treatment is shown in Table 2 and presented in figure 2. The figure 2 shows that the dispersive component of surface energy of Polyimide sheet after plasma treatment is decreased and polar component is increased. But the increase in polar component is higher when compared to corresponding decrease in dispersive component. Therefore, a net gain in surface energy is achieved after plasma treatment. The increase in surface energy is 75% compared to that of the surface energy of Polyimide before plasma treatment.

Table 2. Surface Energy Estimation of Polyimide Surface after Plasma Treatments

Sr .No	Treatment	polar component γ_S^P	Dispersion component γ_S^D	Total surface Energy γ_S	SD
1	Untreated polyimide sheet	36.46$\pm$0.11	20.25$\pm$0.15	56.71	0.09
2	Plasma treated Polyimide sheet	54.41$\pm$0.18	18.12$\pm$0.20	72.640	0.42

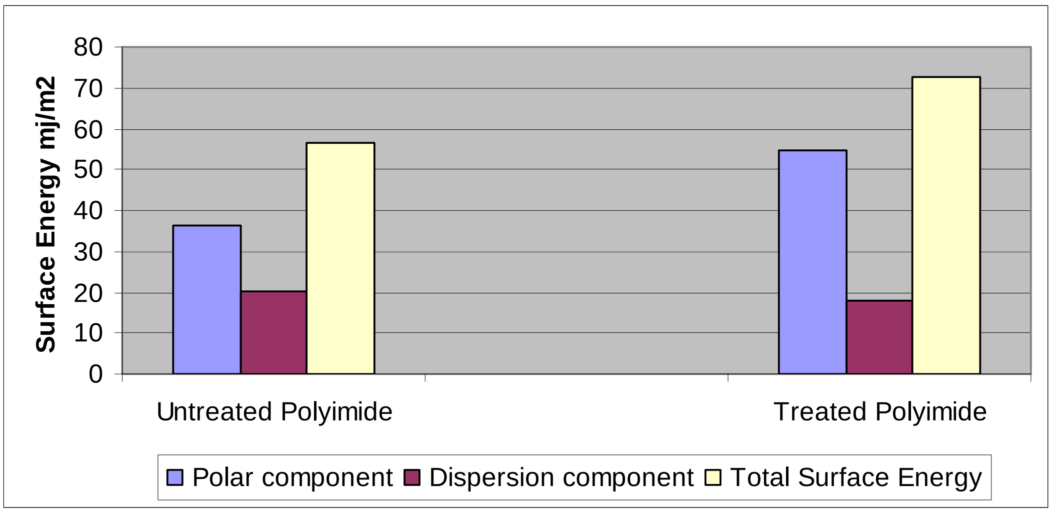

Fig 2. Comparison of polar component, dispersion component, and total energy before and after treatment of polyimide sheet

3.3 Lap Shear Tensile properties of Adhesive Bonded joints

Lap shear tensile strength of untreated Polyimide sheet with titanium and atmospheric pressure plasma treated polyimide with titanium of high performance polyimide adhesive bonded joints was also carried out to compare the adhesive bonded joint strength. A comparison of lap shear tensile strength of Polyimide and titanium bonded joint after modification with atmospheric pressure plasma is given in table 3. Bonded joint strength of atmospheric plasma treated Polyimide sheet with titanium is almost double the strength obtained by untreated Polyimide joint with titanium.

Table 3 .Summery of test results of adhesive bonded joints

Substrate Material	Treatment	Joint configuration	Bonded Area (mm^2)	Failure Mode	Joint Strength (MPa)	SD (MPa)
Polyimide +Titanium	Untreated	Overlap joint	312.5	Adhesive	0.23	0.10
Polyimide +Titanium	Atmospheric Plasma Treated	Overlap joint	312.5	Cohesive failure	3.38	0.07

3.4 Effect of Plasma Treatment on Substrate Surface and Failure Analysis of Adhesive Bonded joints

Surface topography measurements of polymer surface under scanning electron microscope, both prior and post plasma treated Polyimide are shown in figure 3. It is evident from the figure that there is increase in surface roughness of the polymer after plasma treatment and it also essentially helps in improving the adhesion properties of the polymer.

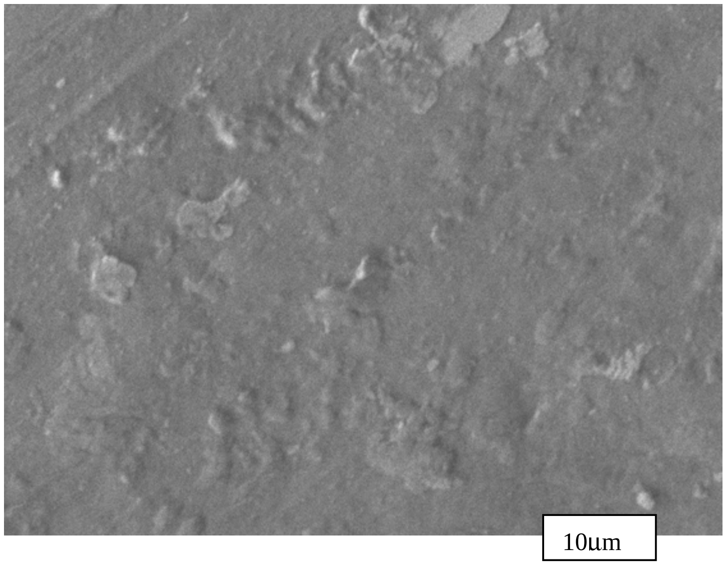

Fig 3(a)

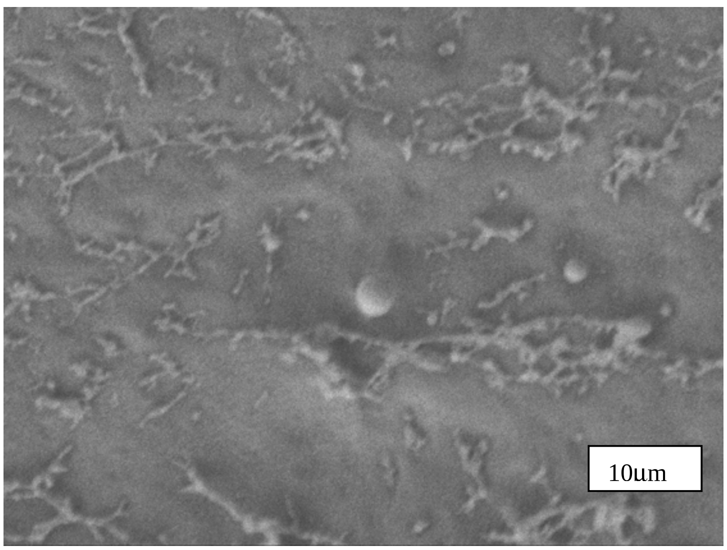

Fig 3(b)

Fig 3.SEM Micrograph of Polyimide Surface before and after plasma treatment

(a) untreated polyimide at 10000X magnification and (b) Treated Polyimide at 10000 X magnifications.

4. DISCUSSION

The present investigation was carried out to justify qualitatively and quantitatively the effect of atmospheric plasma treatment on the surface energy of polymers leading to adhesion characteristics and failure mechanism of adhesive bonded joints. High performance polymers very often do not possess the desired surface properties to form strong adhesive bonds. They are hydrophobic in nature, and in general exhibit insufficient adhesive bond strength due to relatively low surface energy [8]. Therefore, in order to improve the surface energy of polymers, the surfaces of Polyimide specimens were modified by atmospheric pressure plasma treatment. The surface treatment created hydrophilic properties which resulted in increased adhesion. The improvement in adhesion properties is due to the formation of some chemical bonds on the material surfaces [13, 14].Plasma treatment oxidizes the surface of the polymer to such an extent that the adhesive can permeate the roughness of the thin oxidized layer [10]. Relative bond strength improvements of ten to several hundred times are possible depending on the substrate material and gas used for plasma [15]. Surface modification with plasma treatment is confined to the top several hundred angstrom and bulk properties of the material remain the same [8, 15].

Bowditch and Shaw have revealed that when oxygen gas was used to modify polymer surfaces results in hydrophilicity to a polymer surface [1]. It has been emphasized that the desired gas reacts with a wide range of polymers to produce various functional groups, including C-O, C=O and O-C-O at the surface [8, 10]. Adhesion properties are also strongly influenced by the surface topology. Noeske et al and Thurston et al have observed that the surface roughness of polymer samples increases after plasma treatment [9, 14]. The increase in surface roughness attributes increase in adhesion of polymers. In this context, the present investigation also supports this statement as SEM microscopic studies on polymeric surface after atmospheric pressure plasma treatment clearly shows an increase in surface roughness as evident from fig 3. The microscopic roughness can also be attributed to better mechanical interlocking leading to increased adhesive joint strength. However, the most important contribution of atmospheric pressure plasma treatment on the polyimide sheet investigated is the significant increase in surface energy of the polyimide. The polar component of surface energy of the polymers are mainly responsible for the increase in the surface energy of the material due to the formation of the polar functional groups on the surface of the polymers, leading to better adhesion characteristics [14]. The improvement in joint strength with atmospheric pressure plasma treatment could be explained with the fact that atmospheric pressure plasma treatment improves the hydrophilicity. Plasma treatment affects the surface morphology of polymer by increasing the surface roughness. By increasing the treatment time, the surface roughness can be further increased[15].Therefore atmospheric pressure plasma treatment on polymer surface beneficial in two ways, firstly by increasing the surface energy by incorporating different functional groups and secondly by increasing the surface roughness which ultimately provides the effect of mechanical interlocking.

Adhesive bonded joints can fail by a variety of failure modes. After atmospheric pressure plasma treatment, the locus of failure transferred from the adhesive-substrate interface to within adhesive. Therefore, the present investigation concludes with a high note that application of atmospheric pressure plasma treatment is a very effective method to promoting strong adhesion properties of polymers and more precisely for high performance adhesive bonded joints.

5. CONCLUSIONS

The present study has led to conclusions that atmospheric pressure plasma treatment has a significant effect on the surface energies of Polyimide sheet. Formation of functional groups and increased surface roughness after plasma treatment improved the adhesion properties of substrate surfaces, which ultimately increased the adhesive bonded joint strength. Atmospheric pressure plasma treatment results shifting in locus of failure from the adhesive-substrate interface to within the adhesive.

6. REFERENCES

1. M.R. Bowditch and S.J. Shaw, “Adhesive bonding for high performance materials” Advanced Performance Materials Vol.3, (1996) 325-342.
2. M J Shenton, M C Lovell-Hoare and G C Stevens, “Adhesion Enhancement of Polymer Surfaces by Atmospheric Plasma Treatment” Journal of applied Physics D, Vol. 34, Issue 18,(2001) 2754-2760.
3. Alejandro Ureña, María R. Gude, Silvia G. Prolongo,“ Carbon nanofibers reinforced adhesives for joining carbon fiber epoxy composites”13th European Conference on Composite Materials (2008).
4. Custódio J, James Broughton, Helena Cruz, “A review of factors influencing the durability of structural bonded timber joints” International Journal of Adhesion and Adhesives,29(2009)173-185
5. J.Shields, Adhesive bonding, J.Shields, Oxford University Press, London (1974).
6. Leahy W, Barron V, Buggy M, Young T, Mas A, Schue F, McCabe T, Bridge M, “Plasma surface treatment of aerospace materials for enhanced adhesive bonding”, Journal of Adhesion 77 (2001):215-249
7. S. Bhowmik, H. W. Bonin, V. T. Bui, R. D. Weir, “Modification of high-performance polymer composite through high-energy radiation and low-pressure plasma for aerospace and space applications” Journal of Applied Polymer science Vol 102(2)(2006):1959-1967
8. C.-M. Chan and T.-M. Ko, “Polymer surface modification by plasmas and photons” Surface Science Reports, 24(1) (1996):1-154
9. Michael Noeske, Jost Degenhardt, Silke Strudthoff, Uwe Lommatzsch, “Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion” International Journal of Adhesion and Adhesives 24 (2004):171-177
10. Petrie, Edward M.,Hand book of adhesives and sealants,2nd edition, McGraw Hill,Higher Education (1.2007) ISBN 0-07-147916-3
11. Jordan Rotheiser, Joining of Plastics, Handbook for designers and engineers, ISBN 3-446-17418-4
12. Comyn, J., “Contact angles and adhesive bonding.”International Journal of Adhesion and Adhesives,(1992.)12(3):145-149.
13. Ts.O, P. Basic Principles in Nucleic Acid Chemistry.Newyork,Academic Press:1974.
14. Rachel M. Thurston, John D. Clay and Michael D. Schulte, “Effect of atmospheric plasma treatment on polymer surface energy and adhesion” Journal of Plastic Film and Sheeting, 23, (1) (2007) 63-78:
15. Seunghee Han a,Yeonhee Lee a, Haidong Kim u, Gon-ho Kim c, Junghye Lee a, Jung-Hyeon Yoon a, Gunwoo Kim , “Polymer Surface Modification by Plasma Source Ion Implantation” Surface Coatings Technology 93 (1997) 261-4