ADHESIVE JOINING OF POLYMERS REPLACING RIVETTING AND WELDED JOINTS

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
METALLURGICAL ENGINEERING
(With Specialization in Industrial Metallurgy)

CENTRAL LIBRARY
G10933
Date 28.5-02
I.I.T. ROORKEE

By

SHIV KUMAR SINGH

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)

FEBRUARY, 2002

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled "**ADHESIVE JOINING OF POLYMERS REPLACING RIVETTING AND WELDED JOINTS**", in partial fulfillment of the requirement for the award of the degree of Master of Technology in Metallurgical Engineering with specialization in **Industrial Metallurgy**, submitted in the Department of Metallurgical & Materials Engineering, Indian Institute of Technology-Roorkee, Roorkee, is an authentic record of my own work carried out during the period from July 2001 to February 2002, under the supervision of **Dr. Satya Prakash**, Professor, and **Dr. Devendra Puri**, Lecturer, Department of Metallurgical & Materials Engineering, Indian Institute of Technology, Roorkee.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

Shiv Kr. Singh

Date : 25 February 2002
Place : Roorkee

(SHIV KUMAR SINGH)

CERTIFICATE

This is certified that the above statement made by the candidate is correct to the best of my knowledge.

25/02/02

(Dr. SATYA PRAKASH)
Professor
Deptt of Metallurgical &
Materials Engineering
Indian Institute of Technology
Roorkee – 247 667
India

25/2/2002

(Dr. DEVENDRA PURI)
Lecturer
Deptt of Metallurgical &
Materials Engineering
Indian Institute of Technology
Roorkee – 247 667
India

ACKNOWLEDGEMENT

I express my deep sense of gratitude to my guide **Dr. Satya Prakash,** Professor, and **Dr. Devendra Puri**, Lecturer, Department of Metallurgical & Materials Engineering, Indian Institute of Technology, Roorkee, for their keen interest, constant guidance and encouragement throughout the course of this work. Their experience, assiduity and deep insight of the subject held this work always on smooth and steady course. Useful criticism and personal help extended in the hour of need had been immensely useful.

Thanks are due to Dr. Subrat Ray, Professor and Head, Department of Metallurgical & Materials Engineering, Indian Institute of Technology - Roorkee, Roorkee, for providing various facilities during this dissertation.

I am highly thankful to Dr. Shantanu Bhowmik and Dr. S. K. Barthwal, for their continuous help provided during experimental work.

I am also thankful to the Lab Assistant of Materials Engineering Laboratory and Materials Testing Laboratory.

Last but not the least, it is all owed to the blessings of my parents and God that I have come up with this work in due time.

Shiv Kr. Singh

(SHIV KUMAR SINGH)

ABSTRACT

The surfaces of polypropylene (PP) have been exposed to DC glow discharge to enhance wettability of the polymers in order to improve their adhesive joint strength with steel. The surface modification of the polymers have been characterised by measuring contact angles of sessile drops of two test liquids of known surface tension components, such as deionised water and formamide, followed by estimation of their surface energy. The mechanism of surface modification has been studied using Fourier Transform Infrared Spectrophotometer (FTIR). When the polymers are exposed to glow discharge for 60 s at a power level of 25W, the contact angles are found to be reduced from 94 to 60° using deionised water for the PP sheet and 77° to 42° using formamide for the above polymer. Lowering in contact angle at this range results in enhancement in surface energy from 22.80 to 45.51 mJ/m^2 for the PP sheet. It is found that surface energy increases due to the enhancement in polar component of surface energy as polar groups are formed on the polymer surface under exposure to glow discharge as evident from FTIR, which shows negligible oxygen peak for the unexposed polymers; however, glow discharge exposed polymers shows significant oxygen peak. The surface chemistry of the modified polymers, defined as their oxygen to carbon ratio, has been correlated to their adhesive joint strength with steel and it is found that adhesive joint strength of the polymers to steel increases with the increase of oxygen in the polymer surface.

LIST OF FIGURES

LIST OF TABLES

CONTENTS

Chapter 1

INTRODUCTION

In recent years there has been a boom in the industrial use of adhesives. Particularly marked has been the expansion in the field of adhesive for metal-to-polymer joints. This is because of the polymeric materials like high density polyethylene (HDPE) and polypropylene (PP) are progressively replacing the traditional engineering materials like steel and aluminium in fabrication of secondary structures of aircraft, automobiles, railway coaches as well as of many civil construction works due to their superior properties like better corrosion resistance, high strength to weight ratio, relatively low cost and easy recycling. Often these polymeric materials are adhesively bonded to primary metal surfaces, but unfortunately, these polymers exhibit insufficient adhesive bond strength due to their low surface energy. It necessitates surface modification of polymers to enhance their surface energy and to improve their adhesive bond strength [1].

For enhancement of surface energy of polymers like HDPE and PP, several surface modification methods have been developed ranging from wet chemical to dry physical processes such as thermal treatment and electrical treatment by glow discharge or corona discharge under low pressure and atmospheric pressure plasma respectively. Amongst different surface treatments, the low pressure plasma treatment has been found most effective in reference to uniform modification and no chemical hazards [1].

In view of these observations, in this study, the surfaces HDPE and PP sheets have been modified under an optimum exposure to dc glow discharge and the surfaces of the polymers have been characterised by measuring contact angles of sessile drops of two test liquids of known polar and dispersion components followed by the estimation of their surface energies. The mechanism of surface modification of the polymers have also been studied using Fourier Transform Infrared Spectroscopy (FTIR). Finally, the lap shear tensile strength of the adhesive joint of PP with mild steel have been studied using Materials Testing Machine to compare the joint strength of the untreated and surface modified polymers [1].

Adhesion is the phenomenon in which surfaces are held together by interfacial forces. A body that is held to another body by adhesive is called adherend. Substance capable of holding materials together by surface attachment is an adhesive and in general, the term includes cement, glue, mucilage, paste, etc. The location at which two adherends are held together is called a joint.

Adhesive bonding may be preferred as a means of reducing production costs or improving performance even though alternative fastening methods such as rivetting, welding and soldering, etc. are feasible. Adhesive bonding as an assembly method offers cost advantages over other fastening methods as per requirements of dimensions and properties of the components. Unlike other methods, adhesives do not require substrates to be machined (e.g., drilling or rivet or bolt holes) so that over all costs are reduced. However adhesive bonding may involve other expense on equipments for application and curing the adhesive or jigs and fixtures for adherends so that for some assemblies mechanical fastening may be more economic [2].

Adhesive may be required to complement other fastening methods in an assembly. Example of application areas for which adhesive bonding is a practical method of assembly include dissimilar materials like combination of metals, foamed materials, fabrics, wood, ceramics, dissimilar metals which constitute a corrosive couple, e.g., iron to copper or brass, heat sensitive materials, e.g., thermo plastics, acrylics and polystyrene, magnetic materials and glass. Load bearing structures in the aircraft, automotive and civil industries, e.g., clutch facings and brake linings subject to shear are prime examples of automobile applications where adhesive have replaced rivets [2].

In the last five decades, they have replaced the use of screws, rivets, welds, nails, clamping, soldering and brazing in many fields. The major advantages associated with adhesive joints are following :

(1) Adhesive joints allow fabrication of smoother parts and assemblies without breaking through or deforming the surfaces of assembly. This is important aerodynamically for exterior use on aircraft, missile structure, spacecrafts, etc. because reduction of drag permits a smoother flight and also reduced heat generation.

(2) Adhesive bonded joints are light in weight. This characteristic is especially important in aircraft and marine applications.

(3) Adhesive bonded joints distribute the load over large area than in mechanical joints.

(4) There is no need for drilled holes that weakens the structural members.

Adhesive joints serve as passive vibration damper. Adhesives are capable of transferring, distributing and absorbing stress, that often cause fatigue failure in base material. This characteristic is especially important in automobiles, boats and aircraft or other structure that is constantly subjected to severe vibration and shock.

There are several classes, types and groups of adhesives. These have been classified as to use, chemical composition, mode of application, setting factors, vehicle, etc. The first general classifications to be considered are structural and nonstructural adhesives.

1.1 CLASSES OF ADHESIVE USED FOR VARIOUS JOINTS

1.1.1 Structural Adhesives

A structural adhesive would normally be defined as one which can be employed where joints or load-carrying members associated with primary design are required. This type of adhesive will be subjected to large stress loads. The term "structural bonded joints" equates "structural" with the importance of its mission. In this concept, a further definition may be required where "primary structural" means loss of aircraft or vehicle through joint failure and "secondary structural" means severe damage and impairment of the mission. The criteria in many cases have been defined on the basis of bond strength using the arbitrary top value strength of 1000 psi.

1.1.2 Nonstructural Adhesives

These adhesives are not capable of supporting appreciable loads and are generally required to locate parts in an assembly. They will be employed many times where only a temporary bond is required. Their failure would not usually result in the loss of a vehicle. Adhesives, sealants and coatings usually fall into this category, but could be responsible for the full accomplishment of the mission.

1.2 TYPES OF ADHESIVE MATERIALS USED FOR VARIOUS APPLICATIONS

1.2.1 Thermosetting Resins

Thermosetting resins are synthetic organic substances which can be converted by chemical reaction into a permanently hard, practically infusible, and insoluble solid. These resins are high molecular weight polymers which react by polymerization to form hard substances, usually rigid and possessing high strength properties. Thermosetting resins usually have a high modulus of elasticity, do not support combustion and resist the action of most chemicals. When reacted, the thermosetting system will not be liquified by heat but will deteriorate or decompose under heat ranges beyond its limitations. We might compare this to the baking of bread. Once it is catalyzed (baking powder), further baking will only burn it.

1.2.2 Thermoplastic Resins

These resins are often employed in metal and plastic bonding and usually adhere well to both. They do not lend themselves to use as good load-bearing adhesives, especially if they would be subjected to elevated temperatures. They will soften when heated and harden when cooled. An example here would be butter, placed in a molten liquid state by heating and becoming solid upon cooling.

The more common thermoplastic resins include the polyvinyls, acrylics, polystyrenes, cellulosics, and polyamides. They are sometimes used effectively with thermosetting resins for specific formulations.

1.2.3 Elastomeric Resins

These are used widely for modification of the thermosetting systems. They generally fall into a distinct class; e.g., natural and synthetic rubber. A true elastomer is usually defined as a material that will stretch twice its original length without inherent loss of elastic properties. When used as a modifying agent for other resins, they usually induce flexibility and increase peel strength of the systems. They are often used alone or in slightly modified form for sealants, but lack the strength to be used alone for structural applications. Examples of this class are the butyls, nitriles, polysulfides and neoprenes.

1.3 ADHESIVE USED FOR BONDING POLYPROPYLENE

1.3.1 Epoxies

A thermosetting system, 100 percent reactive when in a pure state, the epoxies are very desirable and more widely used than any other chemical type. Epoxy is one of the newer types and has penetrated more fields of manufacturing operations in a shorter space of time than any of its predecessors. The epoxies have been formulated from more materials than any other class. They are very versatile and can be formulated to do any job, limited only by heat. Some formulations will withstand 800°F for short periods. The heat ranges of the epoxies are usually determined by the catalysts utilized to harden the system.

1.3.2 Phenolic Adhesives

The phenolics or phenol-formaldehyde resins are formed by the condensation reaction of phenol and formaldehyde. This material was discovered in 1872. The phenolics are very rigid, strong, and have excellent resistance to fungi. They have moderate to good resistance to moisture, and very good high-temperature properties. The phenolic resins have been used extensively in the lamination of plywood and in filament-wound structures. They enjoy a wider range in the structural-adhesive category when alloyed with other materials.

1.3.3 Nitrile Adhesives

The nitrile rubbers are elastomers and copolymers of unsaturated nitriles and dienes. The nitriles are not used as structural adhesives in this form, but yield many one-part adhesives that are used for bonding small nonstructural parts, especially in the electronics and plastics industry.

Chapter 2

LITERATURE REVIEW

2.1 CHEMICAL MODIFICATION OF POLYPROPYLENE

S. T. Balke [4] deals with free radical initiated controlled degradation of PP. Modification of PP by controlled degradation has been used to narrow down the molecular weight distribution (MWD) and molecular weight averages which in turn affect the properties as a whole. Controlled degradation of PP has been carried out via reactive extrusion using free radical chemistry and has been found to be an effective and economical way of modification since it offers an alternative way to adjust the MWD and molecular weight averages without varying the polymerisation process [1].

Yasuda [5] stated that modification of PP by radical grafting of polar monomer on the PP backbone has led to a sizeable research work. In this process, the polar monomer viz., vinyl chloride, maleic anhydride, methyl methacrylate (MMA) is grafted on to PP backbone in presence of a free radical initiator which is generally a peroxide, e.g., di-cumyl peroxide (DCP), benzoyl peroxide (BPO) in a three component system.

S. Satish [6] in 1980 suggested modification of PP by chlorination, chlorosulphonation, etc. Chlorination provides an important alternative route to modify the PP backbone. PP is an extremely inactive non-polar molecule, because it lacks any reactive site, hence introduction of chlorine atom into the polymer backbone develops polarity into the polymer and this polarity increases with increasing degree of chlorination. Further activating the chlorinated polymer for reaction with different chemicals, viz. thiocarbamates, H_2S may be used to initiate the graft copolymerisation of various monomers, e.g., Vinyl monomers in presence of a peroxide initiator.

Chromic acid is used commercially to etch polypropylene and ABS (Acrylonitrile butadiene styrene) prior to metal plating. It has also been used to treat polyethylene, poly(phenylene oxide), polyoxymethylene, polyether and polystyrene. A typical chromic acid both contains potassium dichromate, water and concentrated sulphuric acid at a weight ratio of 4:4:7.1:88.5.

Chromic acid etching preferentially removes amorphous or rubbery regions. Dramatic improvements of wettability and bondability arise, however, mainly from the complex topography rather than from polar groups introduced by surface oxidation [8].

2.2 SURFACE TREATMENT FOR POLYPROPYLENE

High strength bonds of polypropylene to steel and aluminium can be obtained by dry-heating the faying surfaces to 246 to 273.8°C and pressing the polypropylene on the surface. Adhesion occurs at the surface as the plastic is oxidized. This process is undesirable if tolerances are critical.

Gas plasma treatment of polypropylene can be an effective means of surface treating for adhesive bonding. This is especially true when the acid treatment or treatment by oxidizing flame is impractical or when complex geometric surfaces to be joined. This treatment is accomplished by the surface to an electrically activated inert gas and utilizing a glow discharge tube. Polypropylene surfaces may be prepared for adhesive bonding by the oxidizing flame method, which utilizes an oxyacetylene burner passed over the faying surface until it appears glossy. To ensure that too much oxide is not present on the surface, a light scouring is done with soup and water in order, followed by wash with distilled water and drying at room temperature [7].

2.3 METAL/POLYMER INTERFACE IN ADHESIVE BOND

Published experimental studies are reviewed to verify the validity of the assumption that the columnar and cellular structures, observed at certain polymer/metal interfaces, can be extended to apply adhesive bonded joints. It is shown that such a structure would be consistent with the observed properties and thin joints [8].

2.4 METHOD FOR APPLICATION ADHESION TO A METAL SURFACE

A process for treating metal surfaces to obtain improved susceptibility to bonding with adhesive compositions is disclosed. A metal surface is oxidized with a halogen to form a monolayer of halide ions on the surface. The halide ions are then exchanged with azide ions to form an azide mono layer on the metal surface. Upon contact of the treated surface with an adhesive composition, the azide layer may be thermally or photochemically decomposed to form active nitrene species, which react to bond the adhesive composition to the metal surface [8].

2.5 CORRELATION BETWEEN ADHESIVE STRESS RELAXATION AND JOINT STRENGTH

Generally a cured adhesive absorbs moisture from the ambient environment until it is in equilibrium with the environment at that temperature. When subjected to additional stresses, it will absorb further moisture and establish a new equilibrium. Consequently to long term durability of any adhesive bonded joints is limited by response of adhesive to environmental factors primarily moisture. Indeed the combined strains of temperature expansion and moisture swelling can exceed the elastic limit strain of an adhesive with low temperature and moisture resistance. The strains are further compounded by the effect of sustained loading. Under an army research program the environmental and mechanical response of several adhesive specimens were evaluated concurrently by straining the specimen to failure at predetermined strain in an environmentally controlled chamber.

Correlations between the equilibrium stress-strain behaviour and strength of the adhesives are found excellent joint performance and the mechanism of stress relaxation are discussed [6].

2.6 JOINT STRENGTH OF ADHESIVE BOND

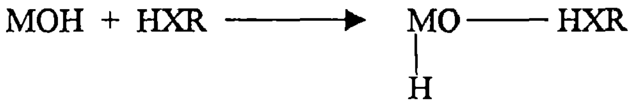
Sadowski [10] suggested that the joint strength depends on a number of factors namely chemical bonding, mechanical interlocking, electrostatic sttraction between the metal and polymer substrates and on the possible formation of weak boundary layers in the region immediately adjacent to the joint interface.

2.6.1 Electrostatic/Electronic Theory

When a polymer is in intimate contact with a metal there is a marked charge separation so that an electrical double layer is formed and the joint is strengthened since work has to be applied to separate the two layers of this capacitor. The contribution of this electrostatic charge force to intrinsic adhesion has been shown to be quite small compared to the contribution from Van der Walls forces (for a system involving adhesion of rubber to a glass interface) [10].

2.6.2 Chemical Bonding

In this case the adherence of the two substrates depends on the formation of secondary bonds (Van der Walls forces, hydrogen bond formation) and primary bonds (ionic, covalent, metallic bonds) through donor acceptor interactions. Impurities (particularly oxygen) on polymer or on metal surfaces have a strong influence on bond line strength. For example, if polyethylene contacting anti-oxidants is used as a hot-melt adhesive, this adheres poorly to a steel surface. The ultra clean metal surfaces prepared in vacuum also exhibit very poor adhesive properties. It shows that satisfactory adhesive bonding eventually depends on the application of conditioning treatments to polymer or metal prior to joining. POlymer surfaces can be acid-etched (in different combinations of sulfuric acid, phosphoric acid and chromic acid) or plasma or corona arc treated to produce reactions (polar) groups that promote chemical bonding during joining operations. Oxide on the metal surface is particularly important since moisture absorption leads to the formation of hydroxyl groups. These hydroxyl groups on the metal surface can react with polar groups in the adhesive as



$$\mathrm{MOH} + \mathrm{HXR} \longrightarrow \underset{\substack{| \\ \mathrm{H}}}{\mathrm{MO}}\text{——}\mathrm{HXR}$$

where M is the metal, H is hydrogen, X is an atom of oxygen, nitrogen or chlorine and R is the polar group [10].

2.6.3 Mechanical Interlocking

When a liquid adhesive is employed, mechanical treatments that increase the surface roughness of the metal produce higher joint strengths. For example Jenigs showed that sand blasting produce higher butt joint tensile strength than grinding, when 6061 aluminium and AISI 304 stainless steel were joined by using a biphenol polyamide adhesive. This improvement in butt joint strengths possibly results surface cleaning, increased contact area for wetting by the liquid and enhancement of energy dissipate mechanisms in the adhesive, when the joint is peeled apart [10].

2.6.4 Weak Boundary Layers

Sadowski Bikerman [10] suggested that failure at the joint interface is improbable and that the presence of weak boundary layer promotes failure adjacent to, but not actually along the interface. It is well documented that the diffusion of lower molecular weight fractions to the outer polymer surface can lead to the formation of weak surface layers.

2.6.5 Effect of Process Parameters on Adhesive Joint

Souney Voyutskil [10] has summarized experimental observations on the bonding conditions and molecular structures of autohesive and adhesive strengths. The bond strength increases with longer contact time, higher chain flexibility, absence of bulky short side groups and lower degree of cross linking. They also favor wetting process.

2.6.6 Effect of Molecular Weight

The increase in molecular weight increases the cohesive strength of materials, and therefore it should favour higher bond strength. But the increased viscosity tends to retard both wetting and diffusion. Thus the effect of molecular weight on bond strength varies depending on material properties.

The bond strength between a polyamide adherend and various butadine-acrylonitrile adhesive increases with decreasing molecular weight of the adhesive.

The bond strength increases with the increase in molecular weight of adhesive like poly (vinyl acetate) on steels, aluminium and cellulose [10].

2.6.7 Effect of Surface Roughness

Surface roughness may increase the adhesive bond strength by increasing the surface area, promoting wetting or providing mechanical anchoring sites. Furthermore weak boundary may be removed during the roughness process.

The bond strength increases with adherend roughness [10].

2.6.8 Micromechanical Interlocking

Mechanical interlocking can produce strong adhesive bonds that are resistant to hydrolytic and thermal degradation. To be effective the adherend surface must have sufficient number of microscopic undercutting or root like cavities.

1. Strong adhesion of the metal plating to the plastics is obtained only when the plastics has been pretreated to produce numerous interlocking cavities.
2. Adhesion to pretreated metals.

Various methods for pretreating of metal surfaces have been reviewed. Many of pretreatments may not only change the surface chemical compositions, but also produce interlocking surface sites [10].

2.7 THERMODYNAMIC CONDITIONS FOR THE WETTING AND SPREADING OF A LIQUID ON A SOLID

The essential physical and chemical variables controlling wetting and spreading have not been recognized nor controlled well enough to permit gathering reproducible and meaningful data. Despite the obvious importance of the subject, the effect of constitution of the liquid and solid on wetting and spreading has only begun to be explored [3].

2.7.1 Contact Angles

Basic to the subject of wettability of the contact angle θ between a drop of liquid and a plane solid surface (Fig. 2.1). When $\theta > 0^o$, the liquid is nonspreading. When $\theta = 0^o$, the liquid is said to wet the solid completely, and it will then spread freely over the surface at a rate depending on the viscosity and surface roughness. Every liquid wets every solid to some extent; that is $\theta \neq 180^o$. In short, there is always some adhesion of any liquid to any solid. On a solid having uniform surface, the angle θ is independent of the volume of the liquid drop. Since the tendency for the liquid to spread increases as θ decreases, the contact angle is a useful inverse measure of spreadability or wettability; obviously, cosine θ is a direct measure.

The roughness r of a solid surface is related to the apparent, or measured, contact angle θ' between the liquid and the surface of the solid and the true contact angle θ (Eq. 2). Here a macroscopic roughness factor r

$$r = \frac{\cos\theta'}{\cos\theta} \tag{2}$$

is defined as the ratio of the true area to the apparent area (or envelope) of the solid.

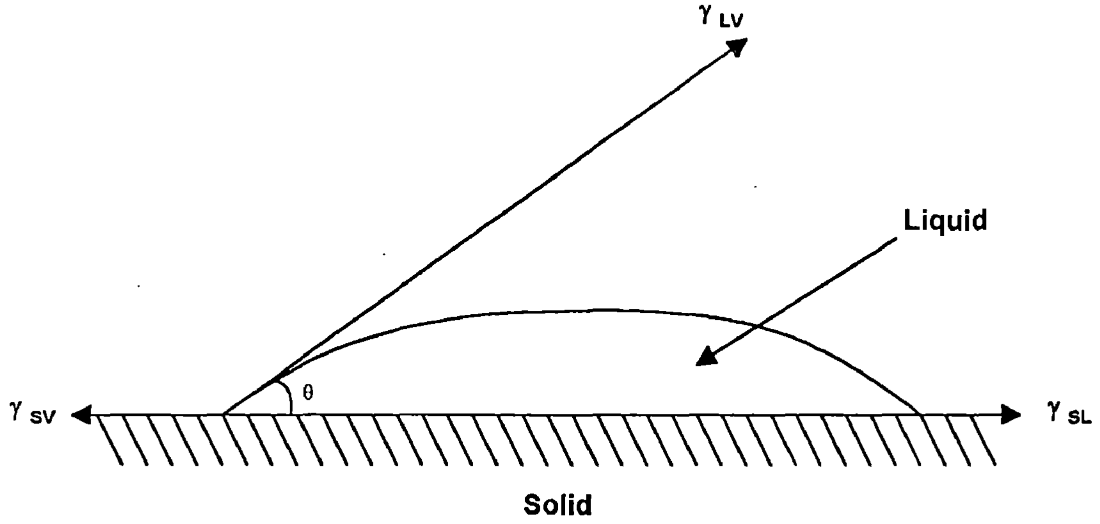


Fig. 2.1 : Liquid Drop in Contact with Solid Surface

This simple relation can readily be shown to be a consequence of the definition of r and the first two laws of thermodynamics. Equation (2) cannot be ignored in practice because surface having r = 1.00 are rare; the nearest to such a smooth surface is that of freshly fire-polished glass. Carefully machined or ground surfaces have values of r greater than 1.5. There are several important consequences of Wenzel's equation. Since r is always greater than unity, when $\theta < 90^o$, equation 2 indicates $\theta' < \theta$. Since most organic liquids exhibit contact angles of less than 90° on clean polished metals, the effect of roughening the metals is to make the apparent contact angle θ' between the drop and the envelope to the metal surface less than the true contact angle θ. In other words, each liquid will appear to spread more when the metal is roughened. When $\theta > 90^o$, equation 2 indicates $\theta' > \theta$. Since pure water makes a contact angle of from 105°-110° with a smooth paraffin surface, the effect of roughening the surface tends to make θ' greater than 110°; values of 140° have been observed [3].

2.7.2 Reversible Work of Adhesion

The three surface tensions γ_{SV^o}, γ_{SL} and γ_{LV^o} existing at the phase boundaries of a drop of liquid at rest on a solid surface (see Fig. 2.1) must form a system in static equilibrium. The resulting relation was also derived using an essentially thermodynamic argument; is led to substituting the various specific surface free energies in the system for the surface tensions. The resulting relation, the Young's equation, is :

$$\gamma_{SV^o} - \gamma_{SL} = \gamma_{LV^o} \cos\theta \qquad (3)$$

Here the subscripts SV^{o} and LV^{o} refer to the solid and liquid in equilibrium with the saturated vapor, respectively. The contact angle used here must be measured at thermodynamic equilibrium.

The reversible work of adhesion per unit area of one liquid with another liquid (or with a solid), is related to the various specific surface free energies as follows :

$$W_A = \gamma_{S^o} + \gamma_{LV^o} - \gamma_{SL} \tag{4}$$

Here S^{o} refers to the solid in a vacuum. If one is interested in the work W_{A*} required to pull the liquid away from the surface leaving the equilibrium-adsorbed film, it is given by the relation :

$$W_{A*} = \gamma_{SV^o} + \gamma_{LV^o} - \gamma_{SL} \tag{5}$$

Eliminating γ_{SL} from equations 3 and 5,

$$W_{A*} = \gamma_{LV^o}\,(1+\cos\theta) \tag{6}$$

From an application of equation 4 to a liquid-liquid interface made up of two layers of the same liquid, the specific reversible work of cohesion W_c of the liquid is found to be simply

$$W_c = 2\gamma_{LV^o} \tag{7}$$

2.7.3 Surface Energies

The surface energy change resulting from the adsorption of the vapor of the liquid on the surface of the solid cannot be generally neglected; they derived the following equation for W_A from equations 4, 5 and 6 :

$$W_A = (\gamma_{S^o} - \gamma_{SV^o}) + \gamma_{LV^o}\,(1+\cos\theta) \tag{8}$$

Here, γ_{SV^o} is the specific surface free energy of the solid immersed in the saturated vapor of the liquid; hence $\gamma_{S^o} - \gamma_{SV^o}$ is the specific surface free energy decrease on immersion of the solid in the saturated vapor of the liquid. The symbol f_{SV^o} will be used to represent this free energy change, i.e.,

$$f_{SV^o} = \gamma_{S^o} - \gamma_{SV^o} \tag{9}$$

Thus equation 8 can be written :

$$W_A = f\gamma_{SV^o} + \gamma_{LV^o}(1 + \cos\theta) \tag{10}$$

Hence from equation 6

$$W_A - W_{A*} = f_{SV^o} \tag{11}$$

The well-known conditions for the spreading of a liquid substance b on a solid (or liquid) substance a :

$$S > O \quad \text{for spreading} \qquad S < O \quad \text{for non spreading} \tag{12}$$

where

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \tag{13}$$

or in the above notation for a solid-liquid system

$$S = \gamma_{S^o} - (\gamma_{LV^o} + \gamma_{SL}) \tag{14}$$

An informative approximation can be derived from equation 14 for the case of an organic liquid spreading upon an organic solid surface, since it is then reasonable to assume that γ_{SL} is negligibly small in comparison with γ_{LV^o}. Therefore,

$$S = \gamma_{S^o} - \gamma_{LV^o} \tag{15}$$

$$\gamma_{S^o} > \gamma_{LV^o} \quad \text{for spreading} \tag{16}$$

Hence in all such systems, when spreading occurs, the specific surface free energy of the liquid is usually less than that of the solid [3].

2.8 SURFACE PREPARATION

It is generally recognized that in order to form an effective adhesive bond, one must start with a clean surface, i.e., a surface from which foreign materials such as grease, dust, dirt, liquids, and loose oxides have been removed. In order to obtain maximum bond strength, a clean surface is usually required in order to produce proper wetting. A simple test for this is to spread water over the surface. A clean surface will hold a continuous, break free water film, a contaminated surface will hold the water in form of droplets of puddles. Since the surface tension of water is higher than that of most plastics, if the water drop spreads over the polymer surface, it can readily be assumed that the adhesive will wet the surface, too. The condition of the joint faces also affects the tensile – shear strength in the adhesion bonded joint. The increase in the tensile shear strength of the combined joints as a result of the pretreatment of the surfaces is attributed to the fact that the tensile-shear face imported by the joint. Until the adhesive fails is greater than that subsequently imported by the spot weld [2].

2.9 EFFECT OF ADHESIVE BOND THICKNESS

Experimental studies have shown that an increase in thickness of adhesive decreases the bond strength. This relationship can be explained in part by the fact that for thinner adhesive layers the greater forces over the interfacial forces (adhesion forces) prevail. Whereas for thicker adhesive layers, the bond strength is determined above all by the cohesive forces of adhesive. It is known that adhesion strength is always higher than the cohesive strength [3].

2.10 EFFECT OF CURING TEMPERATURE AND CURING TIME ON ADHESIVE BOND STRENGTH

For all adhesives there exists a time-temperature relationship, upon which the curing cycle is based. An extension of the curing time or a higher curing temperature (within reasonable limits) is critical and usually results in brittle adhesive layers and reduces the impact resistance of the joints. Below the minimum limits the curing reaction cannot be fully completed and the optimum mechanical properties will not be achieved at all. When curing at room temperature, maximum strength may be attained only after several weeks. Since no two operations (curing temperature and curing time) are exactly alike, it is advisable to conduct always some simple experiments varying both temperatures and cure time to determine the optimum conditions for each particular operation [2].

Budde et al. [11] presented the production and technological characteristics of combined joining technology as well as the strength properties of steel and polymer joints made with weld bonding. With their experimental results, they showed that load bearing capacity of the joint is increased with the use of combination techniques as spot welding or clinching with adhesive bonding. Their results of fatigue tests of an adhesive bond produced by combination is much superior to that of spot welding or clinching bonds.

Heidid et al. [12] in the year 1992 has evaluated five structural adhesives for vehicle stiffening by weldbonding technology. With the aid of his experimental and finite element model studies, he came to the conclusion that the use of adhesive, increased component and vehicle stiffness, possible reduction in the use of spot welds and reduction in the noise levels of a body structure.

Dorn and Georjios [13] have investigated the strength behaviour of adhesive bonded on high tensile steel plates of StE 340 and StE 420 under quasi-state and impact stress. In addition, tension shear tests were carried out with aged specimens (storage under normal climate, storage under water spray testing with sodium chloride solution, outdoor exposure). The results show that the adhesion bonded joints demonstrated good mechanical characteristics under wuasi-static and impact stress. The tests on aged specimens showed that the strength decreased sharply after a relatively short period of time.

J. F. Friedrich [14] put forward a closed procedure for calculating single-lap adhesive bonded polymer sheets of equal thickness. The calculation were based on formulations for single lap bonded joints. A large measure of agreement was found between the theoretical results and results of the test. From the results, it was possible to obtain information on the stresses in the various regions of the joints and to contain guidance in selecting the adhesives for adhesion-bonded which are right for the stress conditions and for the geometry of the workpiece.

2.11 STATIC ANALYSIS OF ADHESIVE BONDED JOINTS

Davies et al. [16] carried a lot of experimental work on adhesive bonded joints made of polypropylene with carbon fibres. They conducted experiments on lap shear specimens and torsional specimens with different surface pretreatments like sand blasting, chromic acid etch and oxygen plasma etch. The results show an improvement in the strength of the joints with acid etching and oxygen plasma treatments.

Chin et al. [17] also studied experimentally the effect of surface pre treatments on the adhesive bonding of polypropylene. They used the surface analytical techniques to obtain a more complete understanding of the chemistry and topography of the pretreated composite surfaces. They conducted experiments for differnet types of pre treatments like solvent wipe, grit blast, peel ply and gas plasma treatment.

It was observed that solvent wiping was not effective in removing contaminations and results in poor bond strength. They concluded that peel ply and oxygen plasma treatment provides good initial bond strength and resistance to hot/wet environments.

Gaghyani et al. [18] studied the mixed mode fracture behaviour of adhesively bonded carbon/epoxy composite joints made by using Araldite as the adhesive. Mixed mode fracture energy of the joint was obtained with different bond thickness using compliance calibration, beam theory and finite element analysis. They investigated the crack path along the bond line using optical microscopy. They investigated that fracture energy depends on both the bond thickness and the actual crack path in the joints.

2.12 DYNAMIC ANALYSIS OF COMPOSITES AND BONDED JOINTS

Moolent et al. [19] conducted fatigue tests on aircraft fuselage repaired by adhesive bonding. He observed a significant increase in the fatigue life of the structure made of adhesive bonding compared to mechanical fastening. He also conducted tests at different environments like hot/wet and NaCl aqueous solutions. He concluded that environment has little effect on fatigue life of such joints.

Kim et al. [20] experimentally investigated the effect of adhesive thickness and adherend surface roughness on fatigue strength of tubular adhesive bonded single lap joint. They also conducted static torsional tests on different types of lap joints with optimal adhesive thickness and adherend surface roughness. They concluded that the double lap joint was the best among the joints in terms of torque capacity.

2.13 SCOPE AND AIM OF PRESENT WORK

The present work undertaken the study of the adhesive bonded lap joint system of polymer to metal using structural adhesive. Tests are conducted on the material testing machine installed in the Materials Testing Laboratory under tensile-shear loading. Shear strength of the adhesive bonded joint under tensile shear loading is obtained and the effect of different adhesives over the shear strength of the joint is investigated.

Undoubtedly, PP because of its low cost and versatile properties enjoys considerable applications in various consumer articles. However, it has limited applications in technologically important fields due to its low surface energy, lack of functionalities, difficulty to spreading of adhesive on polymer surface. So in order to improve the above mentioned drawbacks of PP, an initiative was taken by commercial polypropylene, IITR to modify the commercial PP for enhancing its polar-character.

The route of modification involves low pressure oxygen plasma treatment installed in the Materials Engineering Laboratory. Introduction of oxygen atoms into the PP backbone should make the macromolecule polar and increased polarity makes PP to be polar.

The aim of present study is :

(1) To glow discharge of the commercial PP

(2) To characterise the glow discharge PP so prepared for structural studies by IR for thermal studies by FTIR and by various other characterisations including contact angle.

(3) To look for the possible application of plasma treated PP for spreading of adhesive on the polymer surface.

Chapter 3

EXPERIMENTAL PROGRAMME

3.1 MATERIALS

Commercial polypropylene (PP) sheets of 0.05 mm thickness were used for FTIR studies and the same sheets of thickness 8 mm and mild steel sheets of thickness 1 mm were used for preparation of adhesive lap joints of the polymer to steel. The characteristics of the PP sheets and chemical composition of the mild steel sheet have been shown in Table 3.1(a) and Table 3.1(b) respectively.

Table 3.1(a) : Physical and mechanical properties of the polymer materials used in this investigation

Material	Thickness (mm)	Specific gravity (kg/m^3)	Heat distortion temp. (°C) at 0.45 MPa	Tensile strength (MPa)
PP	0.05 8.0	910	99-110	36

Table 3.1(b) : Chemical composition of the mild steel sheet

C	Mn	Si	P	S
0.19%	0.88%	0.44%	0.034%	0.03%

Two test liquids, such as deionised water and formamide, of known polar and dispersion components of surface tension were used to determine the surface energies of PP through measurement of their contact angles on the substrate by sessile drop method [12, 13]. The known components of surface tension of the liquids are shown in Table 3.1(c).

Table 3.1(c) : Polar, dispersion and total surface tension of the test liquids

Liquid	γ_{LV}^{P} **(mN/m)**	γ_{LV}^{D} **(mN/m)**	γ_{LV} **(mN/m)**
De-ionised water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

The properties of a commercial epoxy adhesive (Araldite AY 105, Hardner HY 840) which was employed to join the polymers with the mild steel has been given in Table 3.1(d).

Table 3.1(d) : Details of Adhesive and Hardner Used

Epoxy adhesive	**Hardner**	**Composition (Adhesive : Hardner) Wt. Ratio**	**Mixing**	**Curing schedule**	**Shear strength of adhesive (MPa)**
Araldite AY 105 (Bisphenol A)	HY 840 (Poly Amidoamine)	1:1	Manual	24 hr at 25°C	7.4-9.8

3.2 SURFACE MODIFICATION OF THE POLYMERS AND MILD STEEL

Schematic diagram of the dc glow discharge set-up, used for surface modification of PP sheet has been shown in Fig. 3.1. The set up consists of a 175 mm high and 150 mm diameter closed glass chamber. Through an inlet, air or other desired gases could be introduced into the glass chamber. A pair of 10 mm thick copper plates of 80 mm diameter were used as anode and cathode inside the glass chamber. The PP sheets were cleaned by wiping with acetone and for FTIR studies the sheets were further cleaned by argon etching and kept on the anode. Inside the glass chamber, a vacuum was created by sucking air with the help of a rotary oil pump having pumping capacity of 12 m^3/h. A pressure of 65.8 Pa, measured by using a Pirani gauge, was maintained inside the chamber. At this low air pressure, dc voltage was applied to ignite the glow discharge in between the electrodes. In this investigation, the dc glow discharge exposure was established at a power of 25 W for a period of 60 s at an electrode spacing of 110 mm. This is an optimum condition of surface modification of the polymers giving rise to their highest adhesive joint strength with steel. Prior to joining, the mild steel surface was also polished by abrading it on 400 grade emery paper and cleaned with acetone.

In glow discharge process of plasma treatment occurs when an external voltage is applied between two electrodes, positioned within a gas mixture at some suitable partial pressure. In this equipment one electrode called the anode as the vacuum retort, is electrically kept at ground potential. The other electrode called the cathode is the workpiece is connected to operate at a negative potential with respect to the grounded vacuum retort. The voltage source supplies a controlled variable voltage. A current limiting resistor permits varying the resistance in the external electrical circuit so that

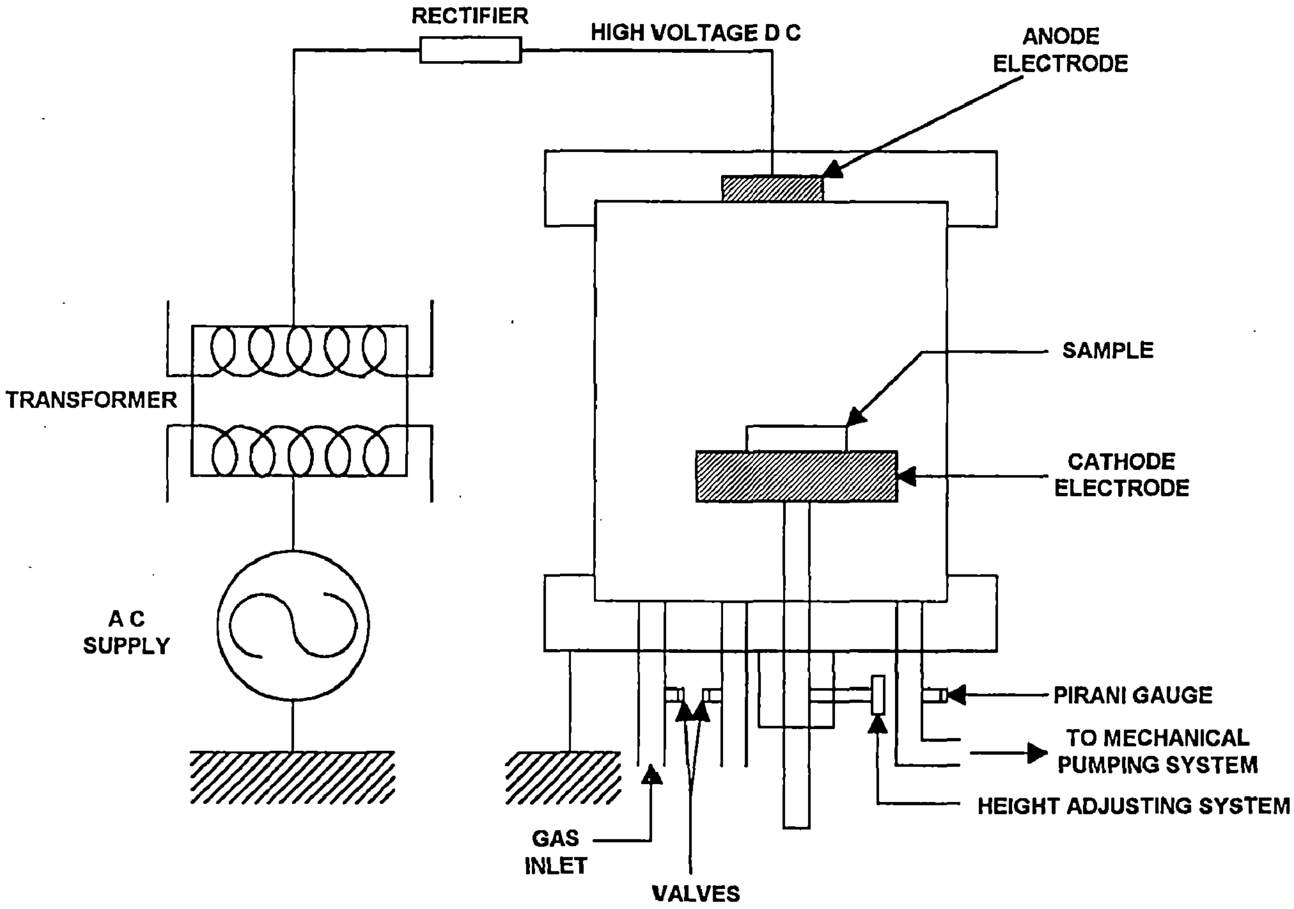


Fig. 3.1(a) : Schematic diagram of the d.c. glow discharge system used

Fig. 3.1(b) : Photograph of dc glow discharge setup

current can be independently controlled at any voltage level. In this equipment the current in the external circuit can be measured as a function of the voltage drop between the anode and cathode.

The medium (gas or gas mixture) for the glow discharge be at a certain partial pressure plays an important role by governing directly to the probability of molecular elements of the gas mixture will be ionized by collision with the electrons travelling from the work surface of the surface to the vacuum retort. The probability of ionization depends upon number of gas molecules present in between the electrodes, which is known as paschen's law.

Plasma treating at a partial pressure of oxygen is called glow discharge oxydiging, ion oxidiging and plasma oxydiging.

The chemical reactions at a work surface, those are believed to be important when a plasma is used as a source of atomic nitrogen, are accounted as follows :

1. Produciton of ionized and neutral nitrogen atoms by energetic electrons

   $e^- + O_2 = O^+ + O + 2e^-$

2. Sputtering of the Fe and contaminants from the work surface by the ionized nitrogen atoms. The impact of the nitrogen ions on the work surface dislodges contamination that can then be removed by the pumping system. This effect called sputter cleaning, removes the significant barrier to nitrogen diffusion from the work surface in to the core.

   O^+ + work surface = sputtered Fe and sputtered contamination

3. Formation of oxide by the sputtering iron atoms and neutral oxygen atoms. Although the predominant mechanism of plasma oxydiging involves this reaction of iron atoms with the oxygen atoms in the gas phase near to the work

surface followed by their redeposition on the surface as a chemical compound, but it is evident that sputtering is not the only reaction mechanism.

It is observed that nitriding takes place even when the energy in the plasma is not high enough to cause sputtering.

sputtered Fe + O = FeO

3.3 CHARACTERISATION OF THE POLYMER SURFACE

3.3.1 Contact Angle Measurement

Contact angles of the de-ionised water and formamide on the untreated and glow discharge treated PP sheets were measured by sessile drop method. The geometry of sessile drop was studied at a magnification of X12.8 under an optical stereo zoom microscope having a cross etched glass graticule fitted with the eyepiece. A vertical and horizontal reference line of the graticule was positioned at the corner of the drop and rotated to make the vertical line tangent to the drop. The extent of rotation was measured using a goniometer which determined the contact angle with an accuracy of 1°. The surface energies of the unexposed PP sheets and the sheets exposed to glow discharge were estimated using the measured contact angles.

Contact angle serves as a criterion of measuring the degree of adhesion between two different materials. Contact angle of a liquid with a solid substrate is defined as the angle at which the liquid boundary touches the surface as shown in the following Fig. 3.2.

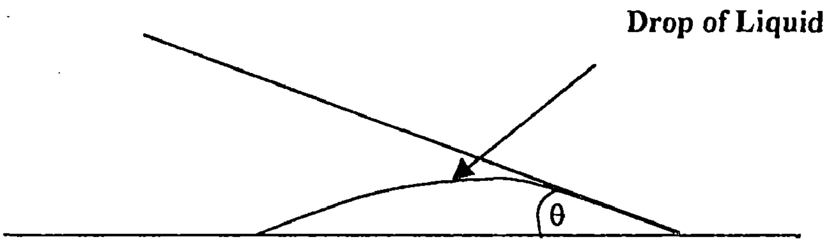


Fig. 3.2 : Contact angle of liquid with solid surface

The concept of contact angle is very important in determining the degree of spreadability of a liquid on to a solid substrate for if a liquid is fairly spreadable on a solid surface, it will touch the surface at a lower angle, i.e., the contact angle will be small. On the other hand, if the liquid does not spread on the substrate, the contact angle for the system will be higher.

3.3.2 Estimation of Surface Energy

The surface energy of a polymer in terms of its components is co-related to the contact angle and surface tension of the test liquid as [14-17] follows :

$$(1+\cos\theta)\gamma_L = 2\sqrt{\gamma_S^D \gamma_L^D} + 2\sqrt{\gamma_S^P \gamma_L^P} \qquad (1)$$

where, θ is the measured contact angle of the test liquid and γ_L is the surface tension of the test liquid with its known dispersion and polar components γ_L^D and γ_L^P respectively. The γ_S^D and γ_S^P are respectively the unknown dispersion and polar components of the surface energy, γ_S, of the polymer surface. The γ_S^D and γ_S^P are estimated by solving the two equations as functions of the measured contact angles of de-ionised water and formamide. The sum of these two components estimates the total surface energy, γ_S, of the polymer surface.

3.3.3 Analysis of the Polymer Surface by FTIR

FTIR were carried out on the untreated as well as glow discharge treated PP sheets. For analysing the samples, FTIR was performed using BIORAD FTS 40. The PP sample substrates were mounted in a specular reflectance cell for collection of (1R-RA) spectra using p-polarization and a 74° incidence angle (Fig. 3.3). The cell is mounted in the front IR beam path of a Nicolet 7199b Fourier transform IR

(FTIR) spectrophotometer equipped with a cryogenic mercury cadmium tellunide (MCT) detector having a frequency range of 5000 to 600 cm^{-1}. Before the sample spectra were collected, a reference spectrum of an An/Al/glass susbtrate mounted in the cell was stored. 1R-RA spectra of the samples were computed from the logarithmic ratios of the sample and reference spectra, for which 1000 intereferometer scans at 2 cm^{-1} resolution were used. Spectra of samples 1 tp 60°C were obtained in situ while being heated in a continuous flow of synthetic air. Spectra of samples heated for various periods of 73, 85 and 100°C ex situ in ambient air (82 kPa) were obtained at 29°C in synthetic air in the cell. Degradative changes in the 1R-RA spectra of the samples were determined by digital subtraction of initial spectra of the samples from spectra collected from various heating times (up to 91 h).

3.4 ADHESIVE JOINT PREPARATION

Prior to preparation of an adhesive joint, degassing of the adhesive was carried out under a pressure of 1 Pa. The use of thick (8 mm) polymer sheet for preparation of the polymer to steel adhesive joint has ensured the remote possibility of failure of the lap joint from either polymer or the mild steel, rather from the adhesive or its interfaces with the polymer and steel. Thus, it provides an opportunity to study the characteristics of the adhesive joint. The lap shear tensile specimens were prepared using the strips of mild steel and polymer sheets of dimensions 110 x 25 x 1 mm and 110 x 25 x 8 mm respectively by applying epoxy adhesive at an overlap length of 12.5 mm, according to DIN 23281 standard, as schematically shown in Fig. 3.4. Any excess adhesive present at the interface was expelled out by rolling the joint at a load of 2 Kg which resulted a joint having adhesive of thickness about 0.2 mm.

3.5 MECHANICAL TESTING

The shear testing test was performed according to S-SERIES (H25 K-S) Materials Testing Machine, at a test speed of 1 mm/min.

The H25K-S Materials Testing Machine is designed with capacity of velocity speed range 0.001 mm/min to 500 mm/min. The set up consists of 1575 mm Height and 650 mm width and 450 mm depth, Maximum crosshead travel excluding grips 1100 mm (Fig. 3.5). The operating temperature is 0°C to 38°C.

According to the Load Cell ZBeam construction conforms to DIN 51221, in the range of 2% to 100%. Accuracy 0.5% of applied force, MTM with a printer connected directly to the H25K-S a test report and high resolution graph (with multiple curve offset) can be obtained within 15 seconds by pressing a single key. Results may be measured and calculated from the printed graph.

3.6 PREPARATION OF ADHESIVE

Commercial Araldite (AY105, Hardner, HY840) was used as an adhesive for the purpose of adhesive bonding of polypropylene and mild steel. Araldite is basically an epoxy base resin used with hardner. The adhesive was prepared by mixing equal amount of epoxy resin and hardner by weight. The adhesive prepared by this process is defined in this investigation as conventional adhesive. After a proper mechanical mixing the adhesive was kept for 5 minutes in a vacuum chamber, having pressure of the order of 65.6 Pa for degassing. The degassing was carried out in order to remove the air entrapped in it, primarily during mixing.

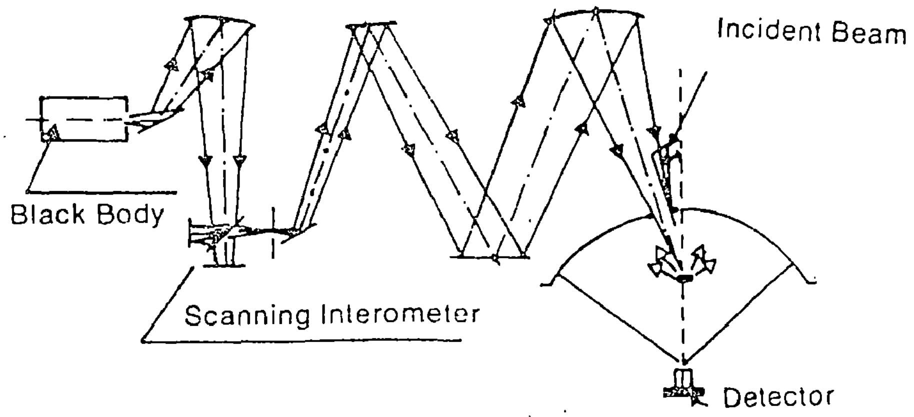


Fig. 3.3 : Optical Schematic of the Infrared Reflectance Spectrophotometer

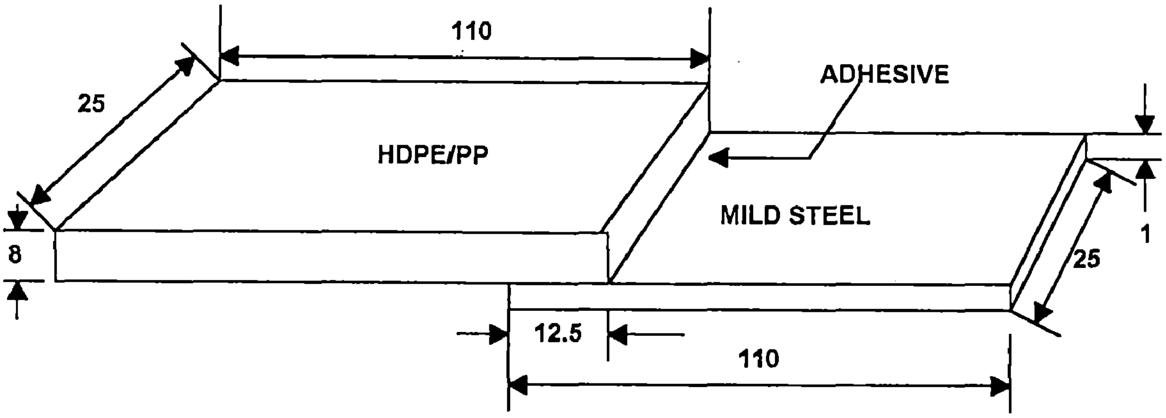


Fig. 3.4 : Schematic diagram of lap shear tensile test spectrum

Fig. 3.5 : S Series (H25K-S) Material Testing Machine

3.7 MEASUREMENT OF ADHESIVE LAYER THICKNESS

The layer thickness of adhesive in the adhesive bonds, prepared by using the conventional adhesive, was measured by polishing the transverse section of the adhesive joints using various grades of emery papers (120, 220, 320, 400, 600, 800 and 1000) from coarse to fine respectively. The specimens were further polished by using grade III alumina powder (0.014 μm) on the polishing wheel having silvyt cloth mounted on it. The polished specimens were studied under an optical microscope. The adhesive layer thickness was measured with the help of optical microscope. The adhesive layer thickness was measured in reference to the applied load of rolling.

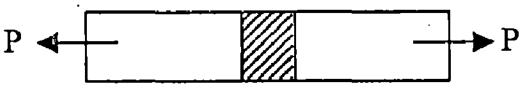
3.8 SHEAR-TENSILE TEST

The shear-tensile test of various adhesive joints between polymer and metal is carried out by uniaxial gripping of the ends of the lap joints. The schematic diagrams of the polypropylene and mild steel joint have been shown in Fig. 3.4. The tests were carried out at a cross head speed of 1 mm/min on a hydraulically operated material testing machine (5 – Series H25K-5). The ultimate shear tensile load was recorded and the failure characteristics of various joints have been studied.

The shear properties of the polypropylene and mild steel prepared at the optimized condition of surface modification (i.e., power of 25W for a period of 60 sec) resulting maximum joint strength were determined at dynamic loading on the materials testing machine. The test was carried out varying the maximum shear stress at given stress ratio of 0.5.

The shear stress (lap) was estimated as

$$\text{Shear strength } (\tau) = \frac{P}{L \times b} \text{ N/mm}^2$$



P = Force (load) , kN

L = Lap length

b = Width of specimen

The sample test data of shear testing are given below :

Lap length = 12.5 mm

Width of Specimen = 25 mm

Shear lap area = L x b

$= 12.5 \times 25 \text{ mm}^2$

$= 312.5 \text{ mm}^2$

Chapter 4

RESULTS AND DISCUSSION

4.1 CONTACT ANGLE MEASUREMENT

4.1.1 Glow Discharge Power

The experimental result of the contact angle of formamide and deionised water of the different power-exposure of the glow discharge treated PP for a given time in 60 sec are given below in Table 4.1.

Table 4.1 : Variation of contact angle with power

S. No.	Glow discharge power	Contact angle (degree)	
		Formamide	Deionised water
1	120	55	68
2	140	51	66
3	150	47	63
4	160	42	60

The Fig. 4.1 reveals that the contact angles of formamide and deionised water on the glow discharge treated PP is minimum for the glow discharge power of 160 V, i.e., 25W. This is an optimum condition of power for the surface modification of the polymers giving rise to the highest adhesive joint strength with steel.

4.1.2 Glow Discharge Time

The experimental result of the contact angle of formamide and deionised water of the different exposure time of the glow discharge treated PP for a given power , i.e., 25W are given below in the Table 4.2.

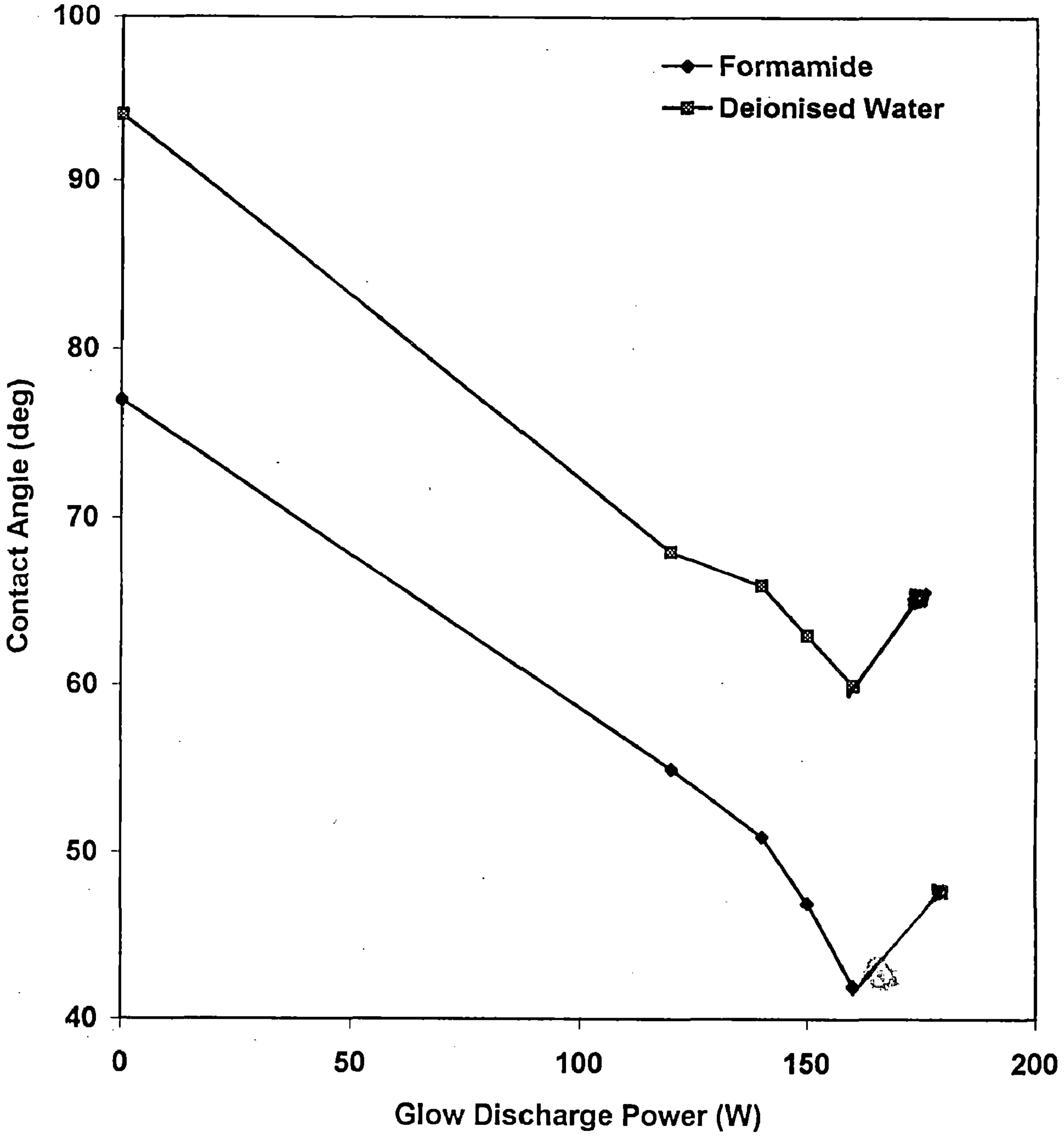


Fig. 4.1 : Minimum contact angle of sessile drop of deionised water and formamide on PP surface treated for different power of exposure of RF glow discharge

Table 4.2 : Variation of contact angle with discharge time

S. No.	Glow discharge time (sec)	Contact angle (degree)	
		Formamide	Deionised water
1	90	44	63
2	60	42	60
3	40	46	65
4	30	48	67

The Fig. 4.2 shows that the contact angles of formamide on the glow discharge treated PP is minimum for the 60 sec exposure. This is an optimum condition of exposure of time of glow discharge treated give high surface energy of polymer giving rise to highest adhesive joint strength with steel.

The Fig. 4.3 shows that the contact angles of deionised water on the glow discharge treated PP is minimum for the 60 sec exposure. This is an optimum condition of exposure of time of glow discharge treated give high surface energy of polymer giving rise to highest adhesive joint strength with steel.

The contact angles of the formamide and de-ionised water on the untreated and glow discharge treated PP are shown in Table 4.3.

Table 4.3 : Variation of contact angle with surface condition

S. No.	Surface Condition	Contact Angle (degree)	
		Formamide	Deionised water
1	Untreated	77°	94°
2.	Glow discharge treated	42°	60°

The Fig. 4.4 reveals that the contact angles of formamide and de-ionised water on the glow discharge treated PP reduce to 42° and 60° respectively as compared to the contact angles of the said liquids observed as 77° and 94° respectively on the untreated surface of PP.

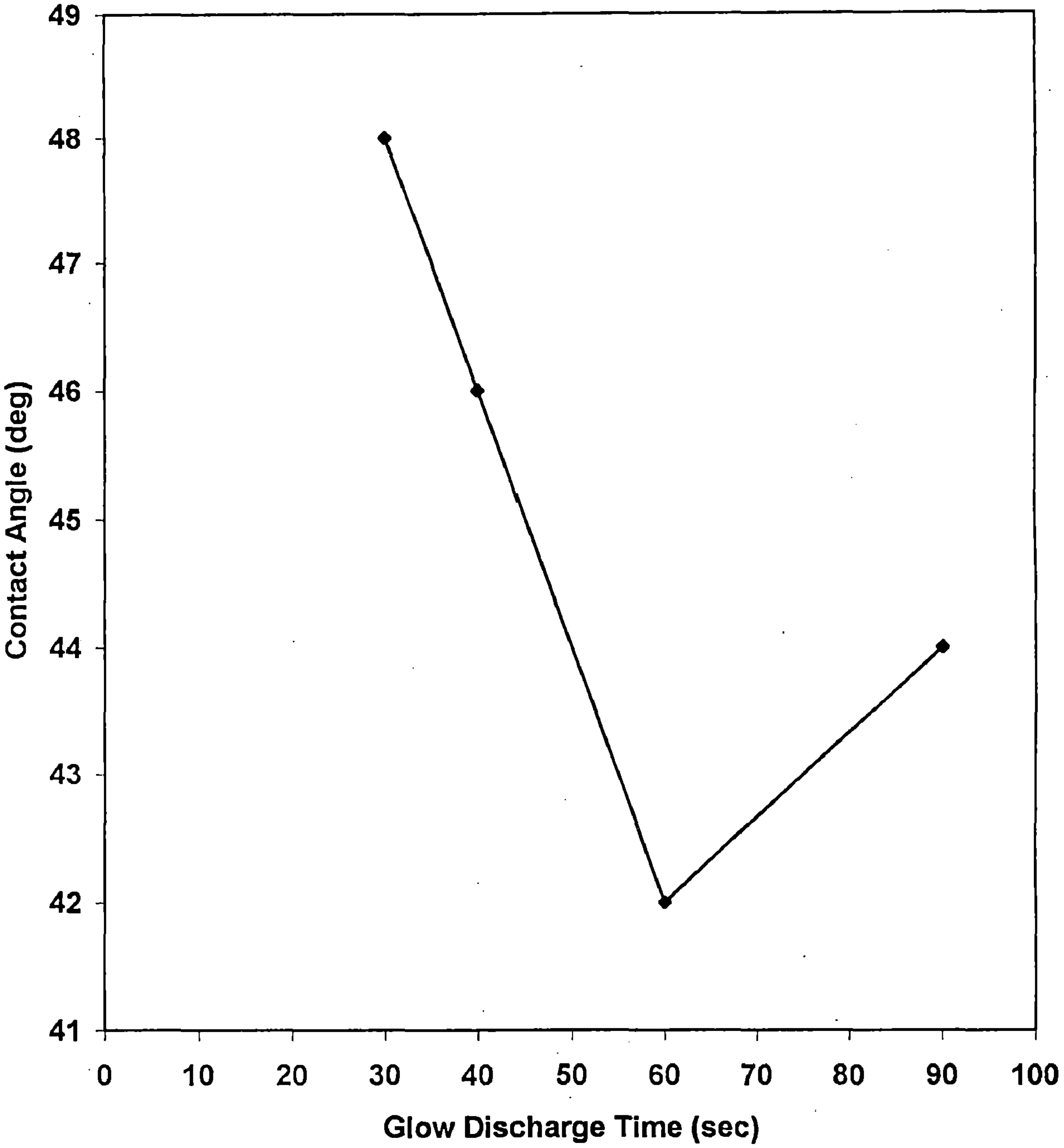


Fig. 4.2 : Minimum contact angle of sessile drop of formamide on PP surface treated for different power of exposure of RF glow discharge

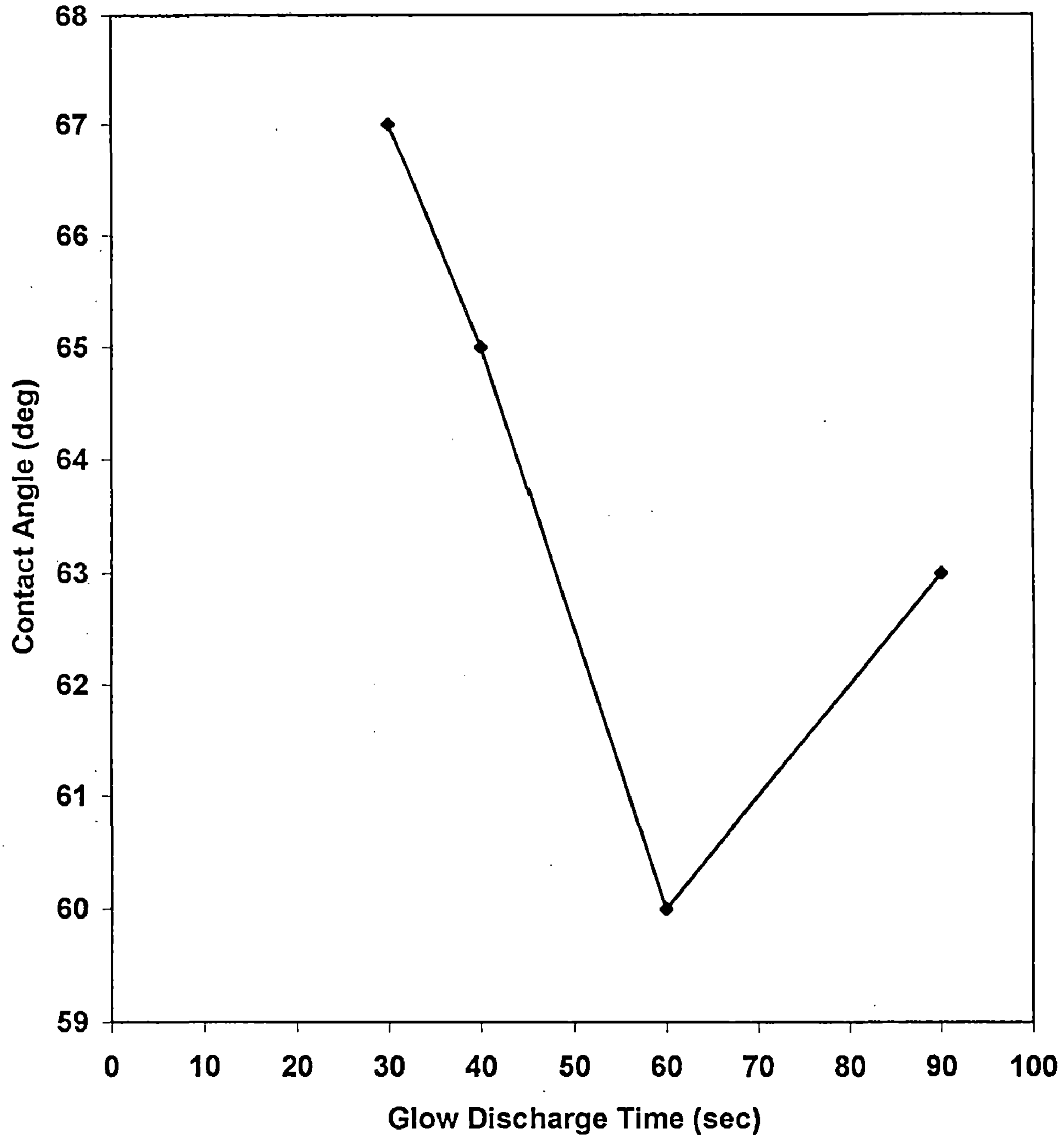


Fig. 4.3 : Minimum contact angle of sessile drop of deionised water on PP surface treated for different time of exposure of RF glow discharge

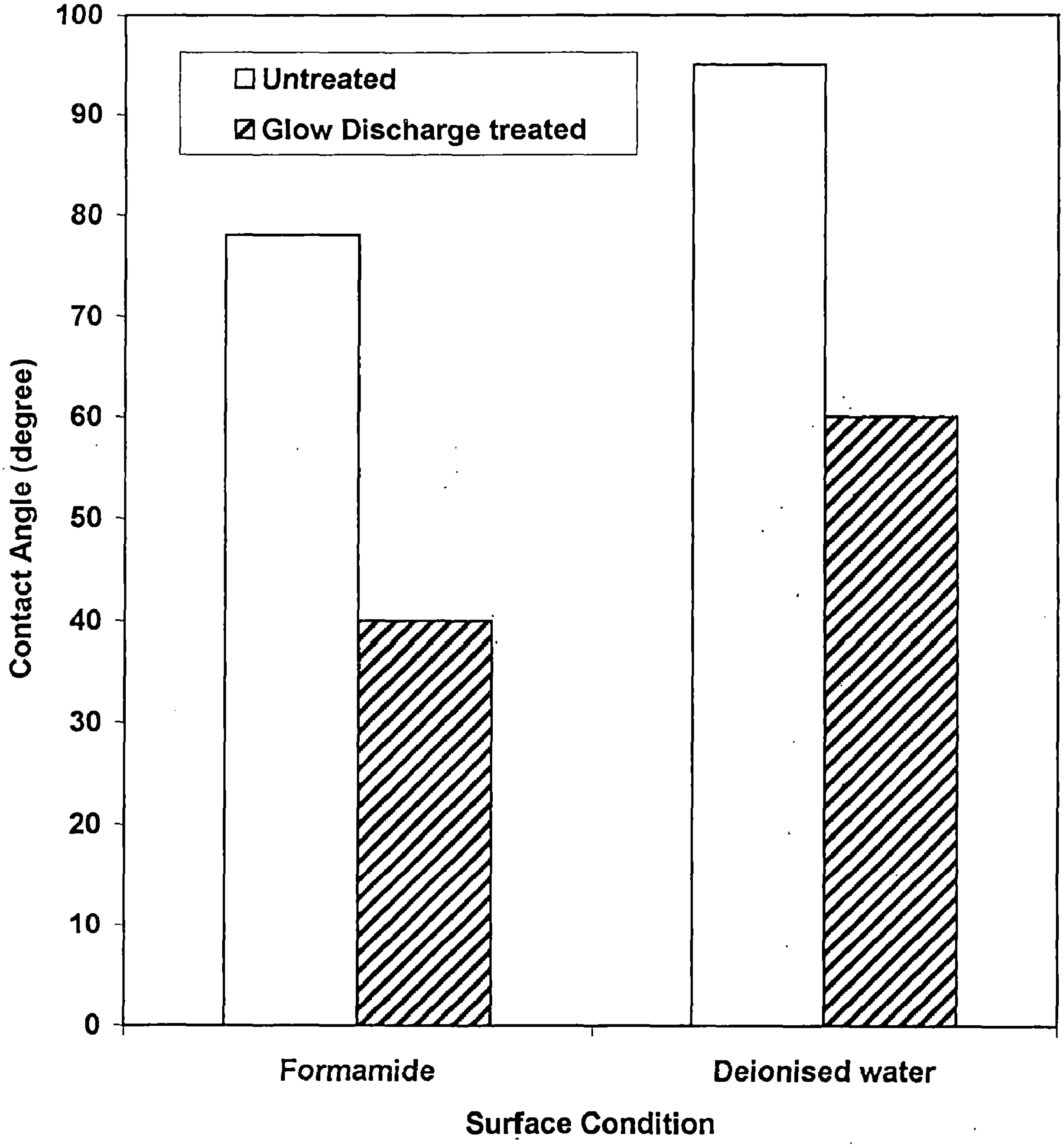


Fig. 4.4 : Change in contact angle of a sessile drop of formamide and deionised water on PP at a glow discharge power of 25W and exposure time of 60s

4.2 ESTIMATION OF SURFACE ENERGY

The polar, dispersion and total surface energies of untreated PP sheets and those exposed to glow discharge have been shown in the Table 4.4.

Table 4.4 : Variation of Polar dispersion and total surface energy with surface condition

S. No.	Surface Condition	Surface Energy (mJ/m^2)		
		Polar	**Dispersion**	**Total**
1	Untreated	3.3	19.5	22.8
2	Glow discharge treated	18.2	27.3	45.5

The Fig. 4.5 reveals that the polar component of surface energy of PP increases significantly due to exposure to the glow discharge as compared to that found in case of the untreated surfaces of the polymers. In case of PP sheet, the dispersion component of surface energy has been found to change moderately with the exposure to glow discharge, where the polar component of surface energy has been found lower than its dispersion component. Due to significant enhancement of polar component of surface energy of the polymers, their total surface energy increases significantly under the exposure to glow discharge as shown in Fig. 4.5.

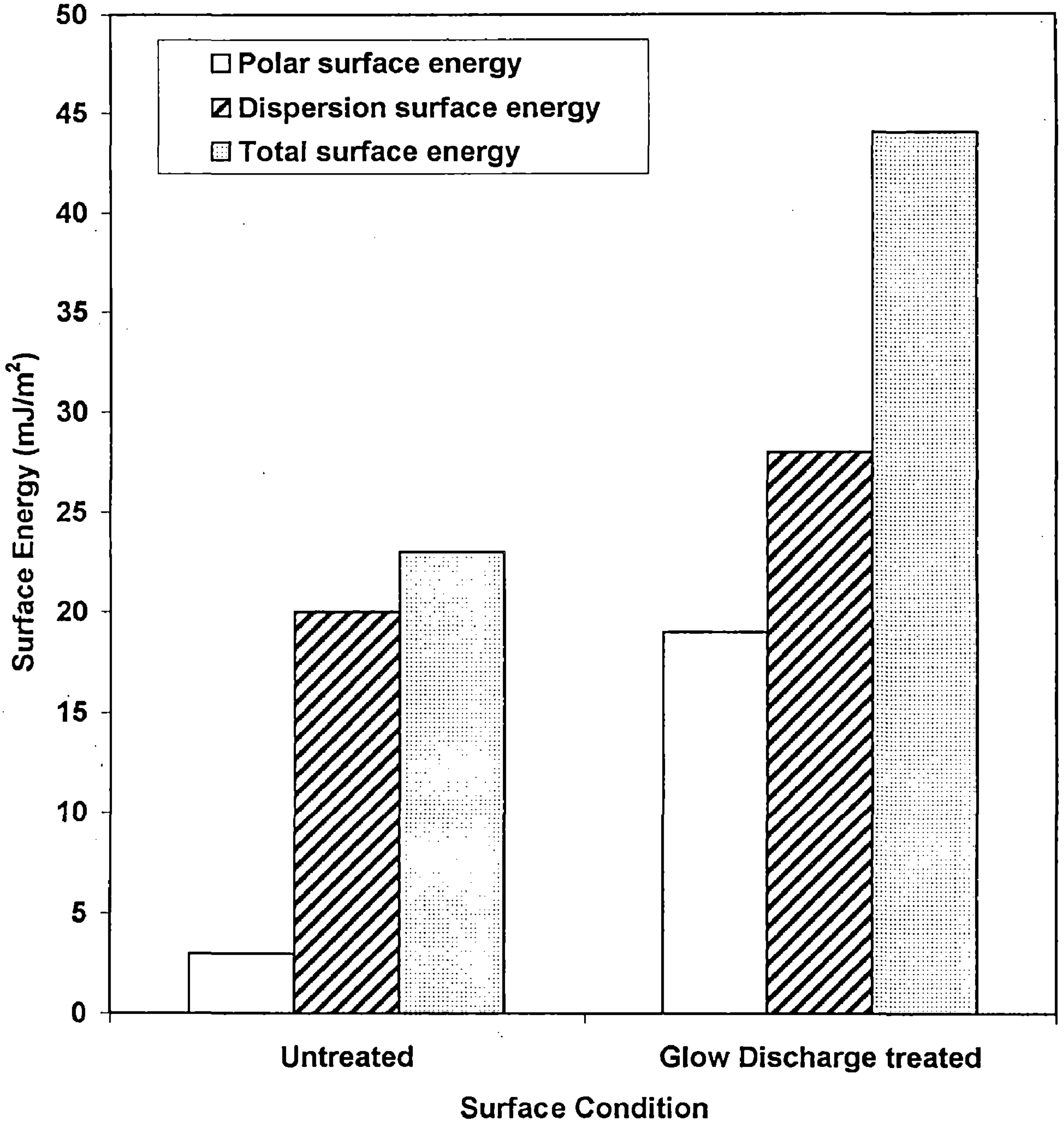


Fig. 4.5 : Change in total surface energy and its two components on PP at a glow discharge power of 25W and exposure time of 60s

4.3 FTIR STUDIES

The survey spectra of FTIR of untreated and glow discharge treated (25W, 60s) polymers are shown in Figs. 4.6 and 4.7 respectively for the PP sheets. The inferences drawn from FTIR studies are tabulated in Table 4.5. From comparative study of spectra of PP and glow discharge PP, new peaks were found in the region 1730-1580 cm^{-1} in the IR spectra of glow discharge PP. These peaks were assigned to the C-O stretching in various groups present in glow discharge PP. Reasonable assignments to various peaks are tabulated in Table 4.5.

Table 4.5 : Inference of FTIR according to wave number

S. No.	Wave No. (cm^{-1})	Inference
1	680-800	C-CI stretching
2	2960-2800 (s)	C-H stretching
3	1485-1340 (w.m)	C-H deformation
4	1300-800 (w)	C-C stretching
5	1580-1730	C=O stretching

The rest of the peaks were similar to that of PP itself. Out of three peaks in C=O stretching region (1580-1730 cm^{-1}), the one at wave no. 1730 cm^{-1} seemed to be due to –CO-O- stretching of (C-O) group and those at 1700 and 1580 cm^{-1} were assigned to >C=O and $-CO_2$ groups respectively. It implied that plasma of PP occurred at all the three carbon atoms, which is further supported by the minor differences in their reactivities. Chlorination of atactic PP has also been reported to proceed via all the three carbon atoms.

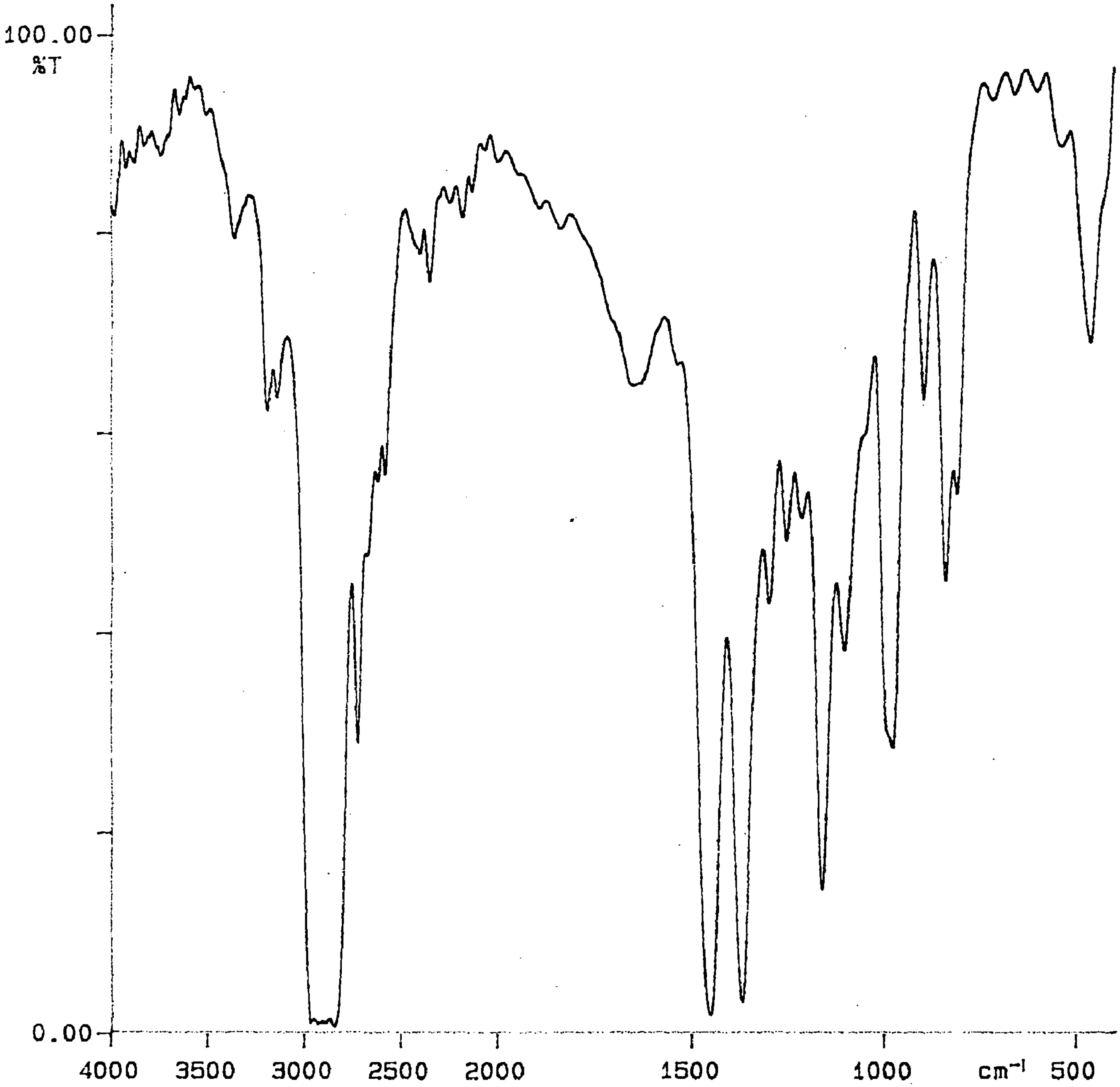


Fig. 4.6 FTIR of untreated polypropylene

G10933.

CENTRAL LIBRARY
Acc. No.........
Date..............
I.I.T. ROORKEE

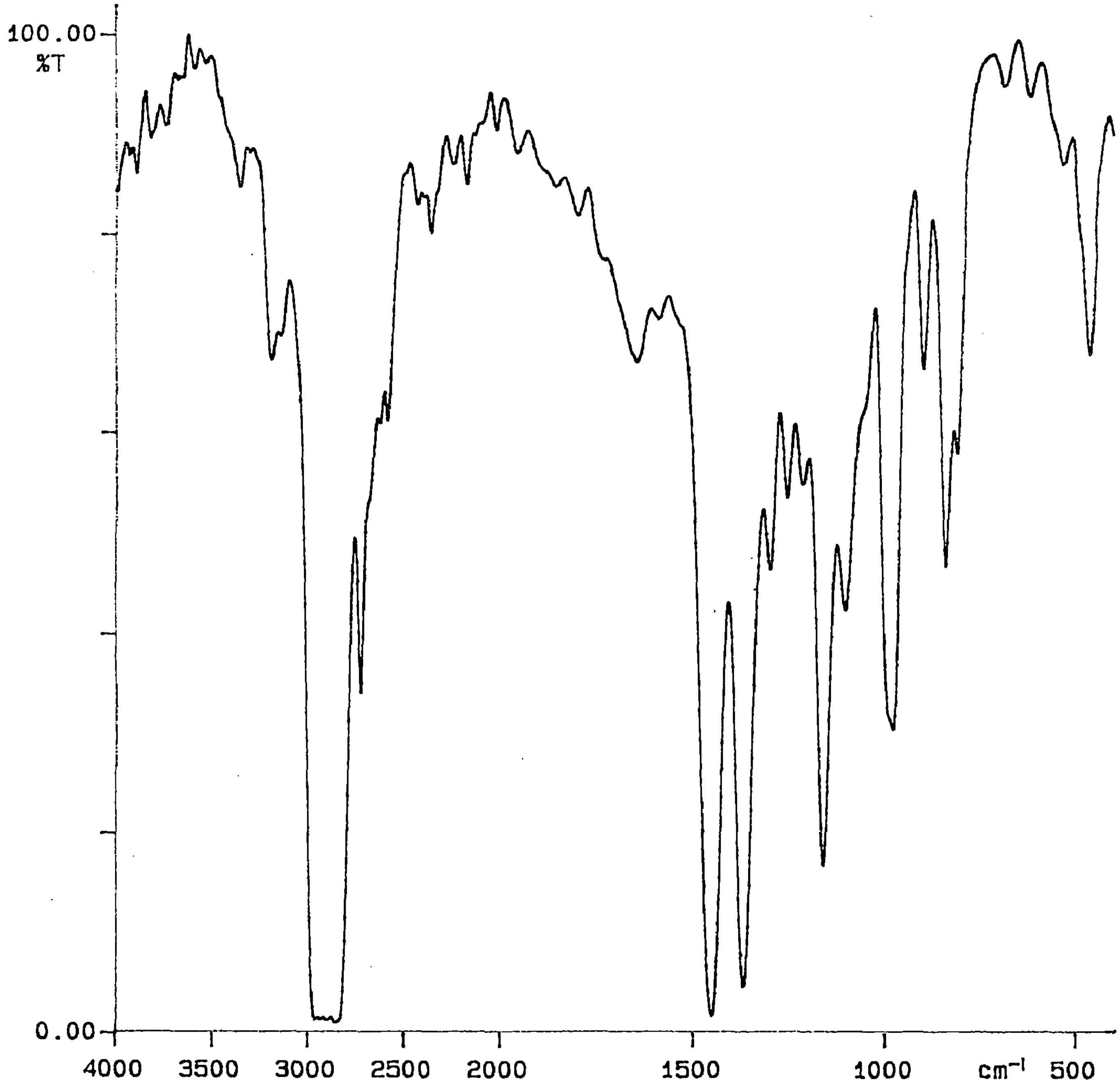


Fig. 4.7 FTIR of glow discharge treated polypropylene

4.4 SHEAR TEST

Specimens with different adhesive were tested in shear. The aim of this test was to find the variation of shear strength of the joint in order to take better choice of the adhesive for shear testing. The results of the shear test are presented in Table 4.6. At the optimum condition of the surface modification of polypropylene (power 25W for a period of 60sec).

Table 4.6 : Shear strength of different adhesives for a given surface condition

S. No.	Adhesive	Shear Strength (MPa)	
		Without glow discharge	With glow discharge
1	Araldite	1.2	4.4
2.	Quickfix	0.3	1.7
3	Flexibond	1.0	1.3

In all the cases failure of adhesive was observed.

The lap shear tensile strengths of the adhesive joints of untreated PP sheets and glow discharge treated PP with mild steel have been shown in Fig. 4.8-4.10. The figure depicts that with the incorporation of oxygen in the polymer surface, adhesive joint strength enhances about 1.3 – 6 times using different types of adhesive.

In case of adhesive using Araldite the lap shear strength of adhesive joint of untreated PP sheet and glow discharge treated PP with mild steel increases 3.5 times as shown in Fig. 4.8.

In case of adhesive using Quickfix the lap shear strength of adhesive joint of untreated PP sheet and glow discharge treated PP with mild steel increases 6 times as shown in Fig. 4.9.

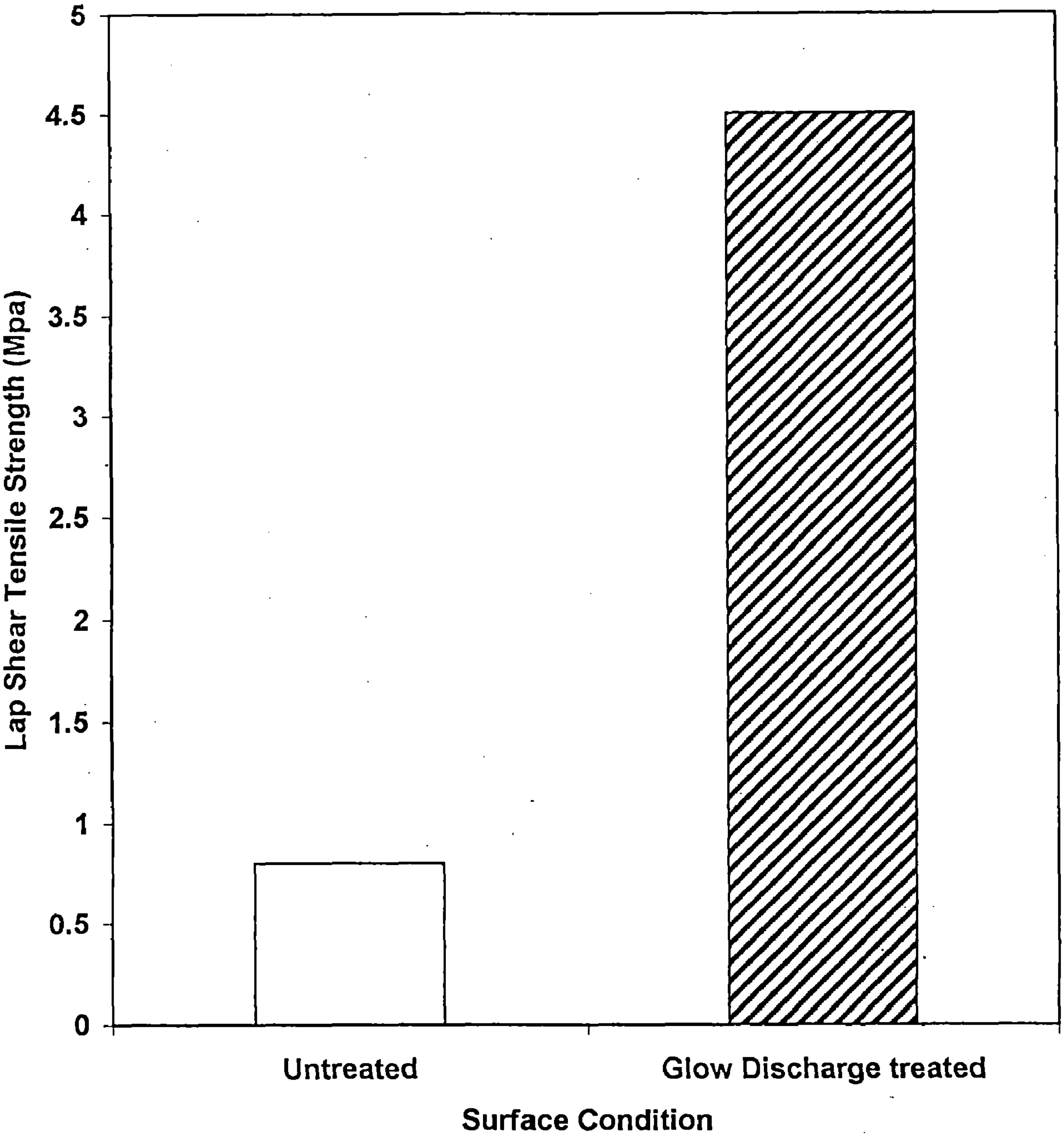


Fig. 4.8 : Change in lap shear tensile strength of PP bonded to mild steel by adhesive
(Araldite AY 105, mixed with hardner HY 840)

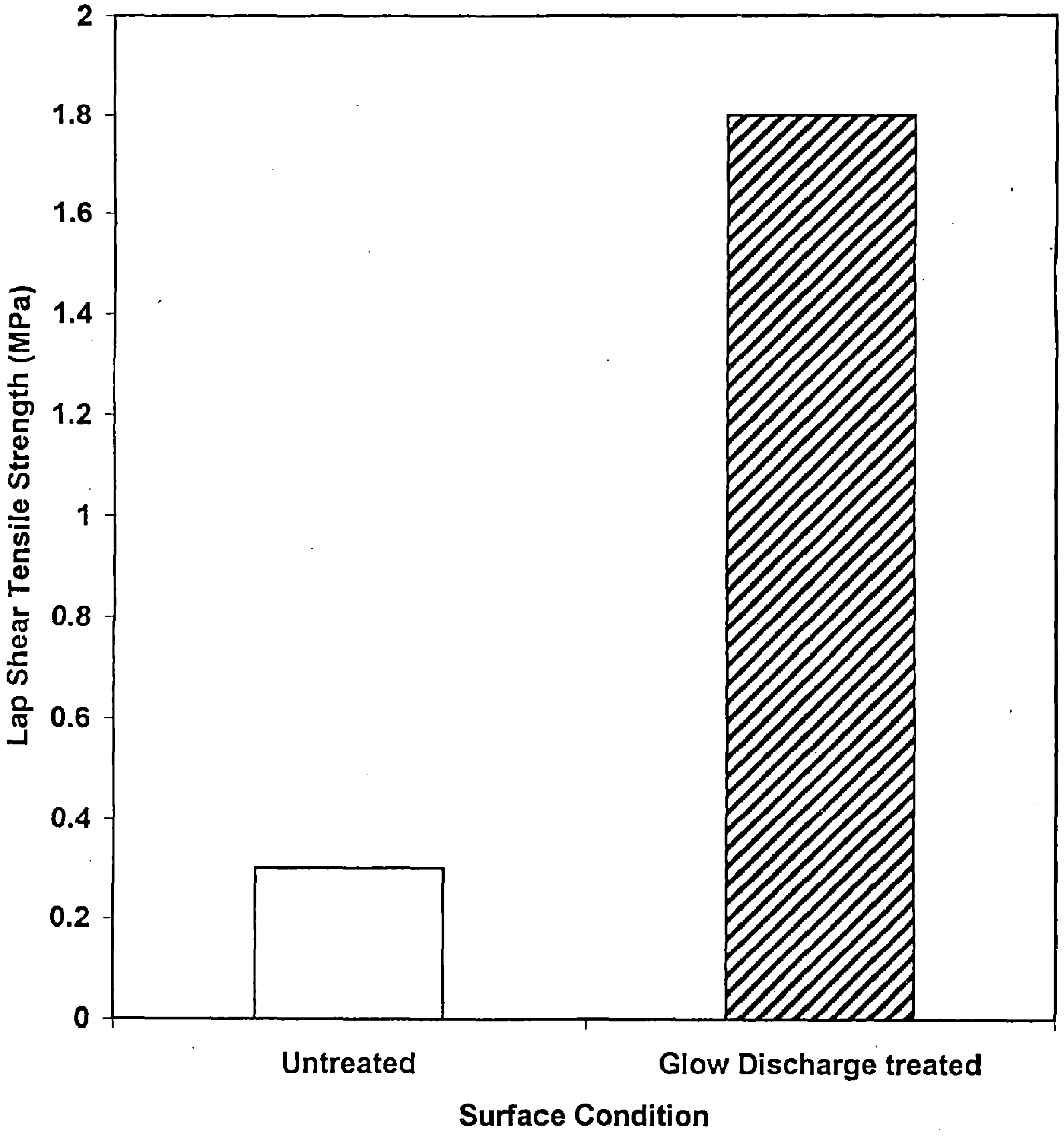


Fig. 4.9 : Change in lap shear tensile strength of PP bonded to mild steel by adhesive (Quickfix E-7)

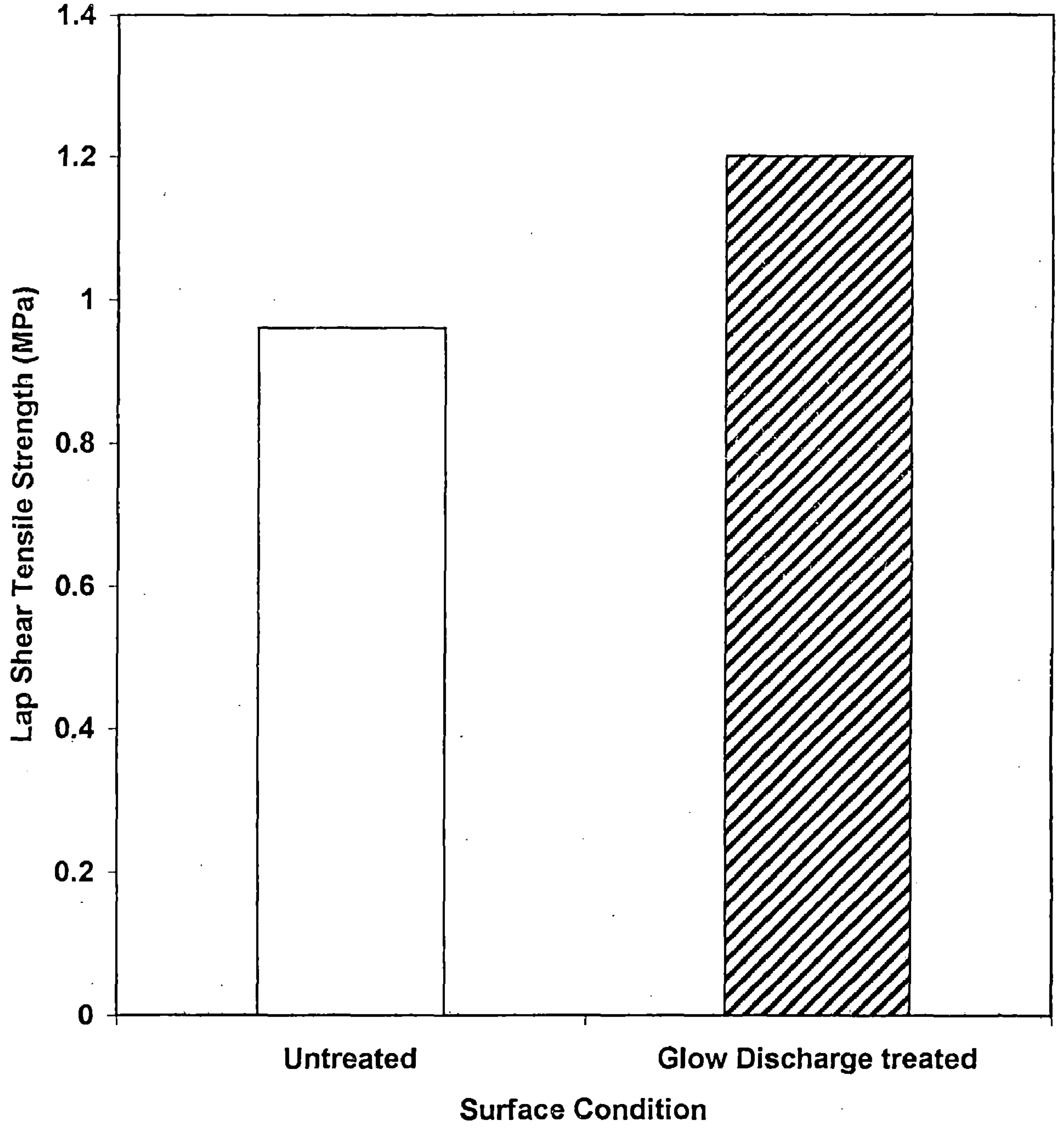


Fig. 4.10 : Change in lap shear tensile strength of PP bonded to mild steel by adhesive
(Fevibond SI19)

In case of adhesive using Fevibond the lap shear strength of adhesive joint of untreated PP sheet and glow discharge treated PP with mild steel increases 1.3 times as shown in Fig. 4.10.

Figure 4.11 shows the adhesive joint of PP to mild steel of different exposure time of glow discharge.

Figure 4.12 shows the failure of adhesive joint of PP to mild steel before glow discharge. Figure 4.13 depicts the failure of adhesive joint of PP to mild steel after glow discharge.

Graphs showing load versus extension using different adhesives for different surface conditions have been shown in Annexure.

4.5 SURFACE CHEMISTRY OF THE POLYMERS AND STRENGTH OF ADHESIVE JOINT TO STEEL

The lap shear tensile strengths of the adhesive joints of untreated PP sheets and glow discharge treated PP with mild steel have been shown in Fig. 4.8-4.10. The figure depicts that with the incorporation of oxygen in the polymer surface, adhesive joint strength enhances about 1.3-6 times. This may be due to the formation of active polar groups on the polymer surfaces by incorporation of oxygen which creates stronger bond with the adhesive. Both the adhesive joints of the untreated PP sheets with steel have been generally found to fail from the adhesive to polymer interface. However, when the polymer surface has been modified by glow discharge, the mode of failure has been found to be complex. In this case, the failure has been found to be primarily contained within the adhesive but at places it is through either the metal-adhesive or the polymer-adhesive interfaces.

Fig. 4.11 : Adhesive joint of PP to mild steel of different exposure time of glow discharge

Fig. 4.12 : Failure of adhesive joint of PP to mild steel before glow discharge

Fig. 4.13 : Failure of adhesive joint of PP to mild steel after glow discharge

The surface energy increases when a polymer surface is exposed to glow discharge as evident from lowering of contact angle of the test liquids. Various authors have reported that contact angle of de-ionised water on polyethylene and polypropylene surfaces decreases significantly due to plasma treatment of the substrates [9]. During surface modification of polymer by low pressure plasma, the polar component of surface energy results from the presence of polar groups on the polymer surface [8] and dispersion component of the surface energy arises from the dispersion forces of the Heitler-London type [9]. The absence of polar groups on the untreated PP sheets is indicated by a very low polar component of the surface energy. It is observed [7] that the polar component of surface energy of polymer improves significantly with a short exposure to plasma, however, the dispersion component of surface energy remains almost unaffected. It is also reported [8] that polar component of surface energy remains almost unaffected. It is also reported [8] that polar component of surface energy increases significantly when plasma treatment is carried out at 750 V for 450 s. The present investigation depicts (Fig. 4.5) that the polar component of surface energy of PP sheets increases significantly upon exposure of glow discharge and the dispersion component of the surface energy remains more or less unaffected. FTIR investigations by Friedrich et al. [14] have demonstrated that the oxygen functionalisation of the PP surface on exposure to oxygen plasma leads to the presence of C-O, C=O and COO- groups on the surface. The oxygen content of the surface increases to wave number 1500-1710 cm^{-1}, when exposed to pure oxygen plasma for 3 min at 60W. Harth and Hibst [15] observed that 60% of the oxidised carbon atoms are bonded as C-O, roughly 30% of carbon atoms are bonded as C=O, and the rest are bonded as carboxyl functionalities. Similar kinds of trend has also been observed in present investigation.

Similar functional groups on the polymer surfaces may have resulted after glow discharge treatment to enhance the oxygen content. Yao et al. [7] have reported that the adhesive joint strength of PP to stainless steel was increased about 10 times when the PP was treated for 2 min at 60 W under argon plasma and Guezenoc et al. [15] have reported that the strength of adhesive joint of untreated PP to mild steel was 0.7 MPa and increased to 2.1 MPa when the PP was treated to air plasma and similar kind of trend has also been observed in present investigation.

Chapter 5

CONCLUSION & SCOPE OF FUTURE WORK

CONCLUSION

In the present investigation, the effect of surface modification and surface chemistry of PP sheets by DC glow discharge and their adhesive joining to steel has led to the following conclusions :

(i) Glow discharge exposure for 60s at a power level of 25W, on the PP sheet reduces the contact angle of formamide and de-ionised water significantly compare to the untreated PP sheet.

(ii) Glow discharge treated PP sheet shows higher polar and total surface energies over those observed for the untreated PP sheets. However, the dispersion component of surface energy remains more or less unaffected.

(iii) Glow discharge treated PP sheet shows significant increases the functional groups, as well as lap shear tensile strength of the adhesive joints of the PP with the mild steel.

SCOPE OF FUTURE WORK

1. Various other types of polymer may also be tried for making adhesive joint.
2. Various other types of metals may also be tried for making adhesive joint.
3. Various other types of adhesives may also be tried for joining of metal to polymer.
4. Other techniques may also be applied for analysis of the polymer surface.

REFERENCES

1. S. Bhowmik, P. K. Ghosh, S. Ray and S. K. Barthwal, *J. Adhesion Sci. Technol.*, 12, 1181-1204 (1998).
2. Charles V. Cagle, "Handbook of Adhesive Bonding", McGraw Hill Book Company, New York (1968).
3. Shield J., "Adhesives Hand Book", The Butterworth Group (1968).
4. R. Rew, S. T. Balke, *J. App. Polym. Sci.*, Vol. 35, p. 1033-1034 (1998).
5. H. Yasuda, B. Sherry, *J. Appl. Polym. Sci.*, Vol.27, 1735 (1999).
6. Y. N. Sharma, S. Satish and I. S. Bhardwaj, *J. App. Polym. Sci.*, Vol. 26, 3213 (1981).
7. Y. Yao, X. Liu and Y. Zhu, *J. Adhesion Sci. Technol.*, 7, 63-75 (1993).
8. J. Schultz, A. Corre and C. Mazeau, *Intl. J. Adhesion Adhesives*, 4, 163 (1984).
9. C. M. G. Carlsson and K. S. Johansson, *Surface and Interface Analysis*, 20, 441-448 (1993).
10. Ramanatham G., Liberthi C.H.M., Sadowski M. M. and North, "Joining of Polymer to Metal", Vol. 21, 382 (1994).
11. L. Budde et al., "Adhesive Bonding in Combination with Spot Welding and Clinching", Welding in the World, Vol. 30, No. 1/2 , 1992.
12. Heidid et al., "Weldbonding of Structural Adhesives for Body Stiffening", SAE 92218, 1992, pp. 155S-159S.

13. Dr. Dorn et al., "Adhesive Bonding and Spot Weldbonding of High Strength Steel Plates – Strength Characteristics of the Joint after Ageing", Schwessen and Schneiden, 1988, pp. E8-E10.

14. J. F. Freidrich, P. Rohrer, W. Saur, Th. Gross, A. Lippitz and W. Unger, *Surface Coating Technol.*, 59, 371-378 (1993).

15. H. Guezenoc, Y. Segul, S. Threy and K. Asfardjani, *J. Adhesion Sci. Technol.*, 7, 953-965 (1993).

16. Davies P. Cantwell, W. J. Jar P. V. Bourban P. E., Zysman V. and Kausch H. H., *Journal of Composites*, Vol. 22, pp. 425-426 (1991).

17. Chin W. J. and Wightman P. J., *Journal of Composite Structures*, Vol. 15, pp. 419-420 (1995).

18. Gaghyani H. R. and Mai Y. W., *Journal of Composite Materials*, Vol. 30, pp. 1248-1250 (1996).

19. Moolent L., Bridgeford N., Rees D. and Jones R., *Journal of Composite Structures*, Vol. 21, pp. 121-122 (1992).

20. Kim K. S., Kim W. T., Lee D. G., Journal of Composite Structures, Vol. 21, pp. 163-164 (1992).

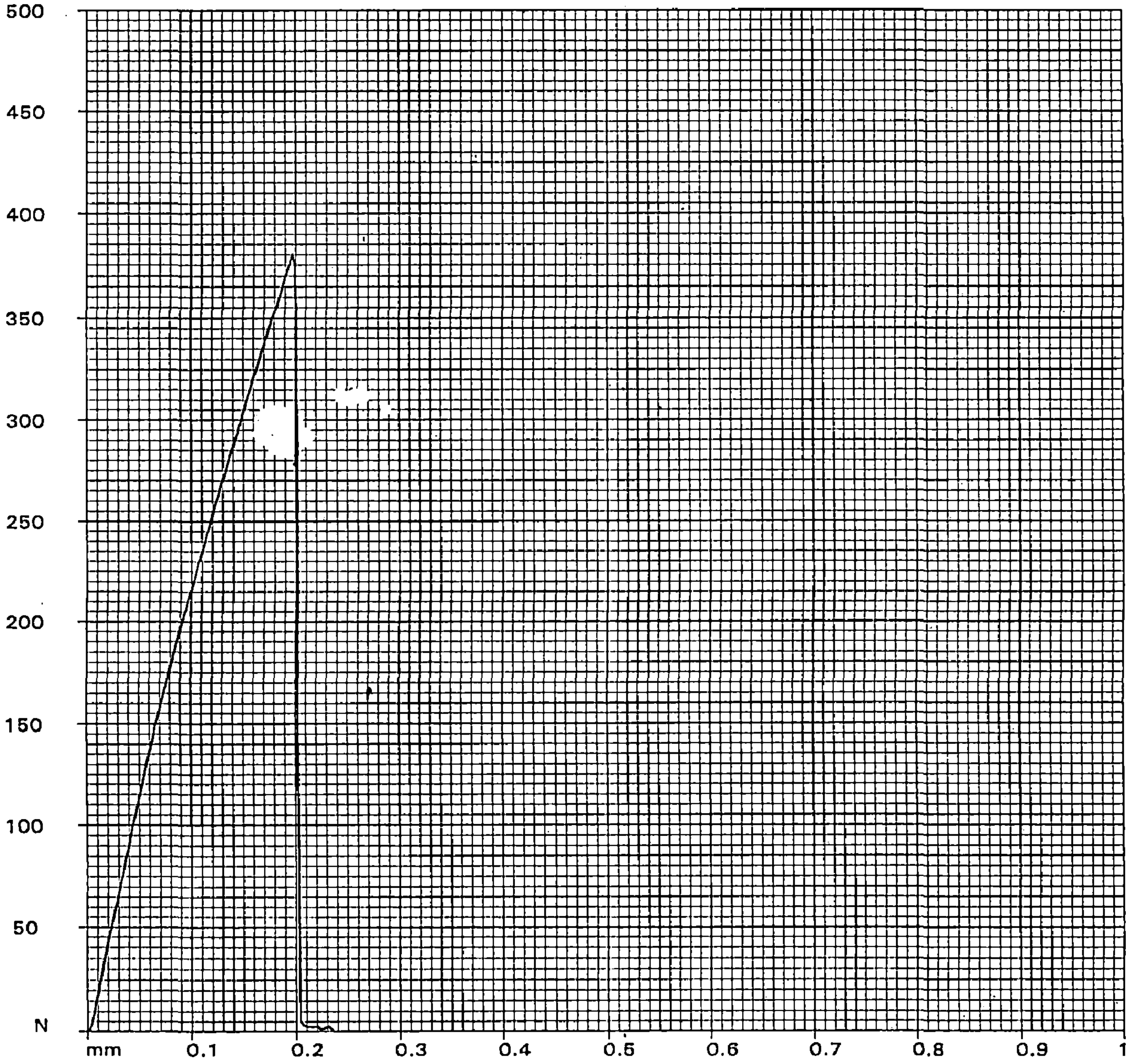
ANNEXURE

```
                    ********************
                        Hounsfield
                        Test Report
                    *********************

      Product Code ... PP
      Date ..........: 4.1.2002
      Batch Number ..: A/W
      Operator ......:
      Test Speed.....:     1.000{mm/min}

----------------------------------------------------------------------------------------
        Max      Break      Ext @ Brk    1.000      2.000      3.000      4.000      5.000
        N        N          mm           N          N          N          N          N
----------------------------------------------------------------------------------------
1       380.833  -1.666     0.234        0.000      0.000      0.000      0.000      0.000
----------------------------------------------------------------------------------------
```

Fig. A-1 Plot between load and extension using Araldite without glow discharge for metal to polymer joint

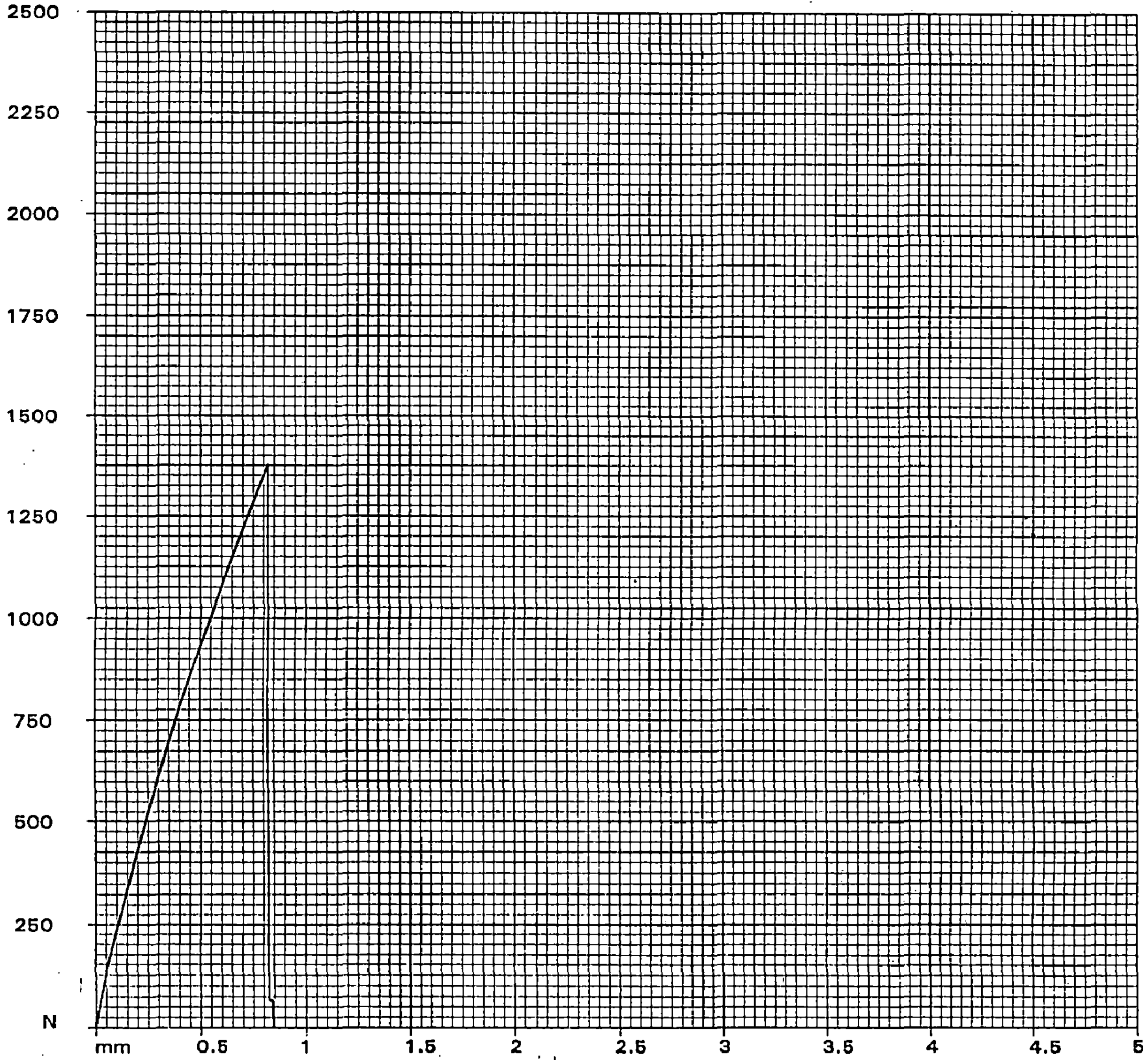


```
          ********************
              Hounsfield
              Test Report
          *********************

     Product Code ... PP
     Date ..........: 4.1.2002
     Batch Number ..: A
     Operator ......:
     Test Speed.....:     1.000{mm/min}

----------------------------------------------------------------------------------------
        Max     Break       Ext @ Brk    1.000     2.000     3.000     4.000     5.000
        N        N            mm          N         N         N         N         N
----------------------------------------------------------------------------------------
1    1380.000  -67.500      0.844       0.000     0.000     0.000     0.000     0.000
----------------------------------------------------------------------------------------
```

Fig. A-2 Plot between load and extension using Araldite with glow discharge for metal to polymer joint

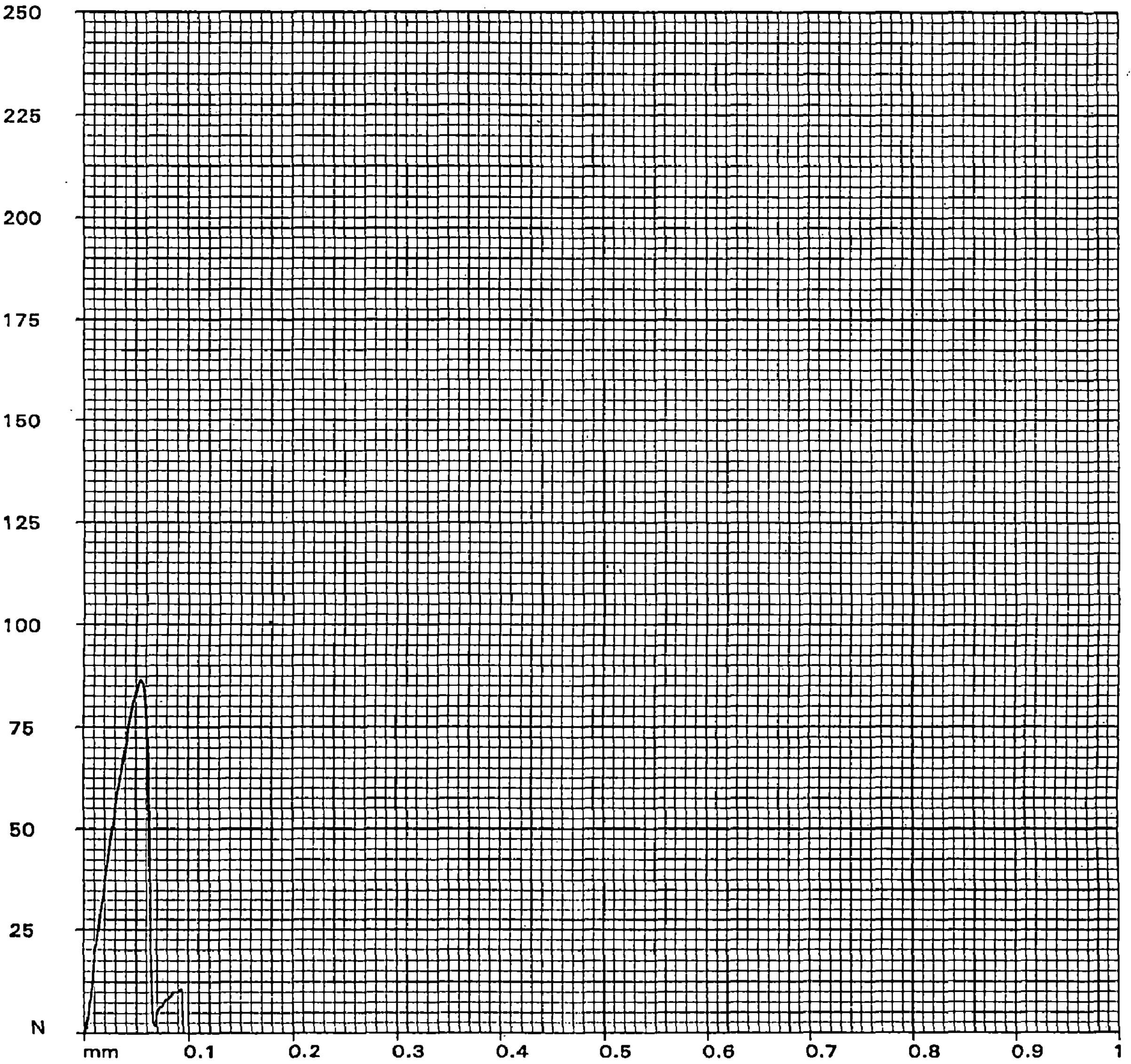


```
                    ********************
                        Hounsfield
                        Test Report
                    ********************

       Product Code ... PP
       Date ..........: 4.1.2002
       Batch Number ..: Q/W
       Operator ......:
       Test Speed.....:     1.000{mm/min}

    ---------------------------------------------------------------------------------------
         Max     Break     Ext @ Brk    1.000     2.000     3.000     4.000     5.000
          N        N          mm          N         N         N         N         N
    ---------------------------------------------------------------------------------------
1       86.666   -10.833     0.094      0.000     0.000     0.000     0.000     0.000
    ---------------------------------------------------------------------------------------
```

Fig. A-3 **Plot between load and extension using Quickfix without glow discharge for metal to polymer joint**

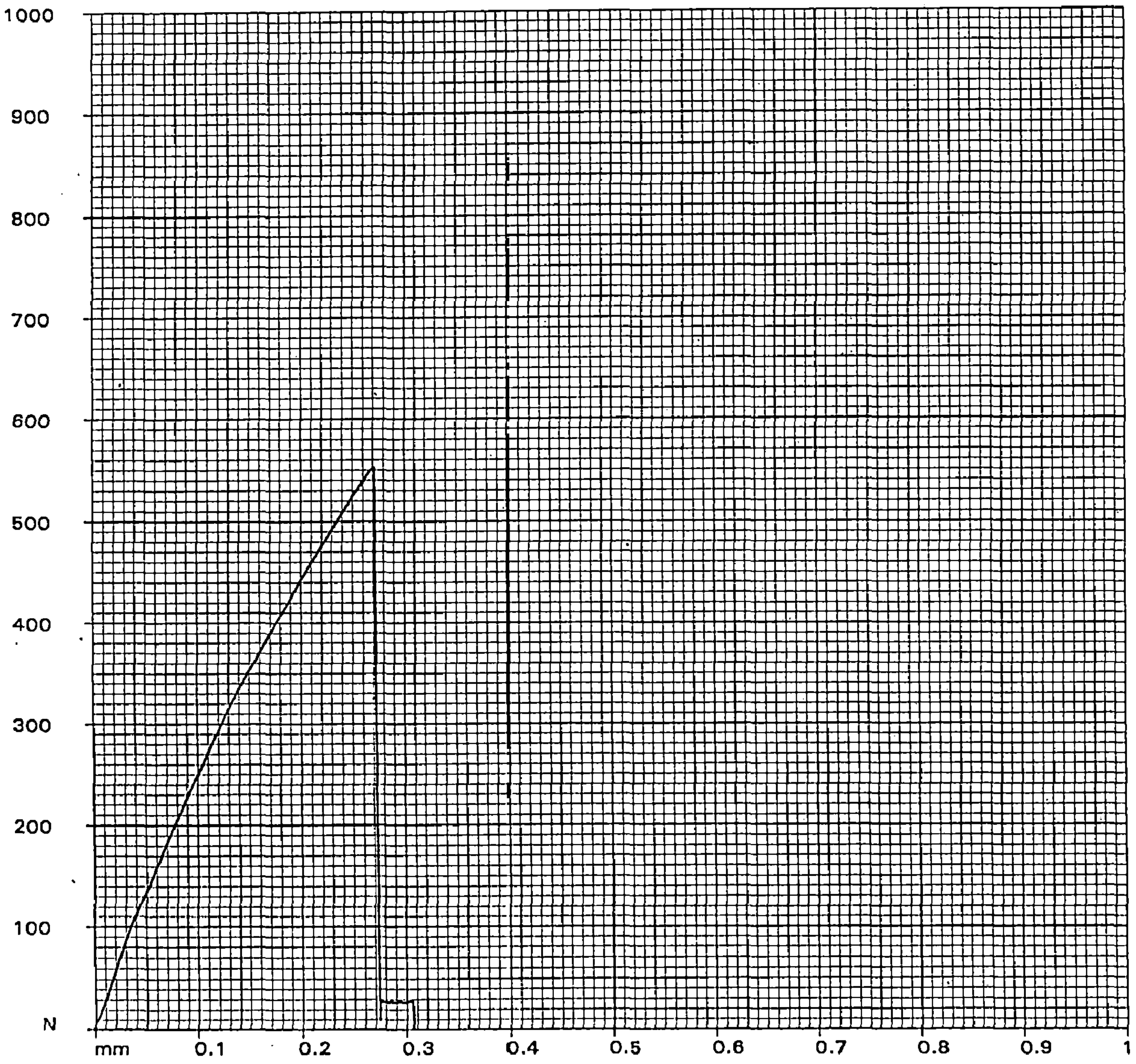


```
                        ********************
                           Hounsfield
                           Test Report
                        *********************

        Product Code ... PP
        Date ..........: 4.1.2002
        Batch Number ..: Q
        Operator ......:
        Test Speed.....:    1.000{mm/min}

 ----------------------------------------------------------------------------------------
      Max       Break      Ext @ Brk    1.000     2.000     3.000     4.000     5.000
       N          N           mm          N         N         N         N         N
 ----------------------------------------------------------------------------------------
 1   553.333    -28.333     0.306      0.000     0.000     0.000     0.000     0.000
 ----------------------------------------------------------------------------------------
```

Fig. A-4 Plot between load and extension using Quickfix with glow discharge for metal to polymer joint

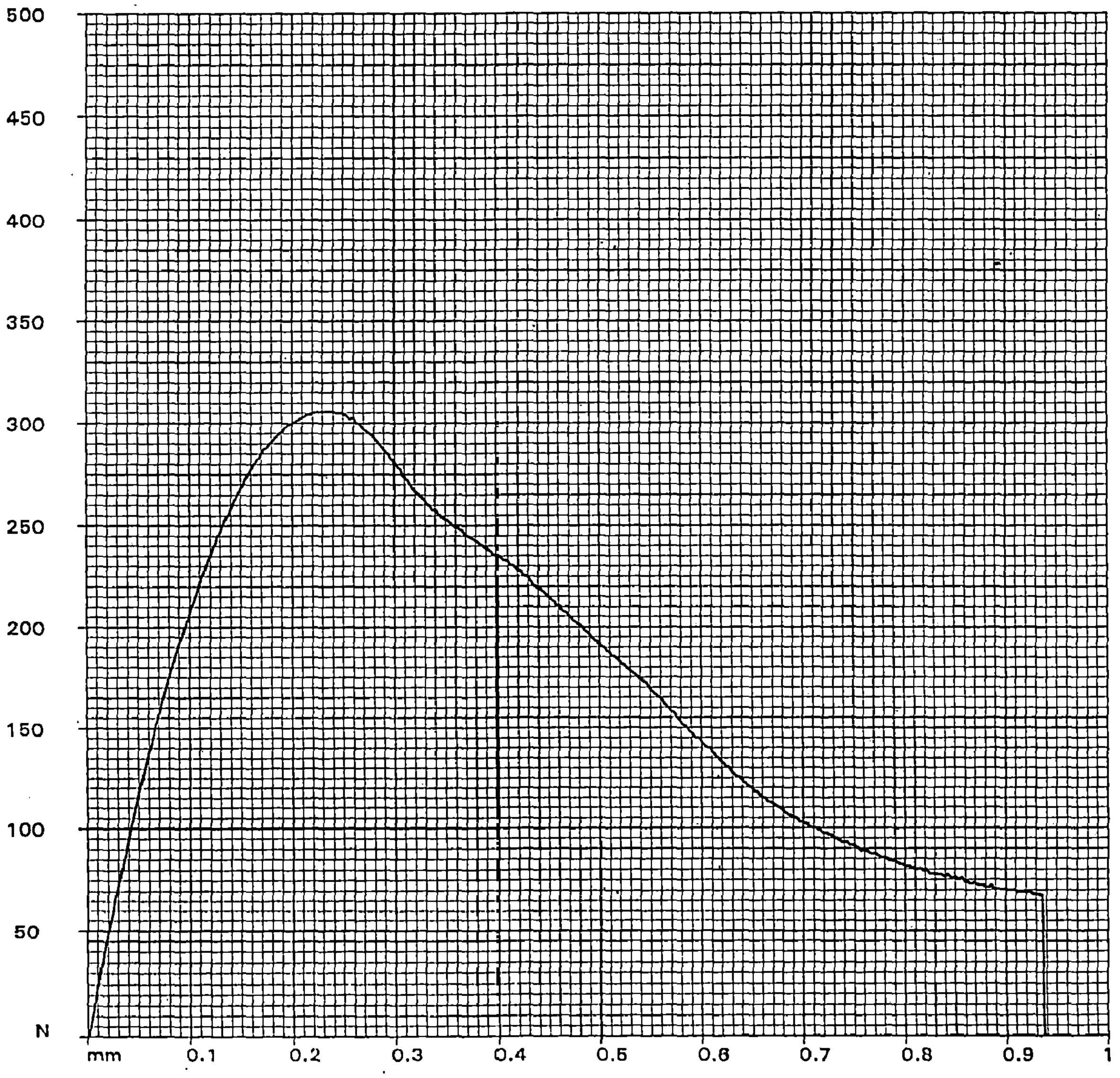


```
                    *********************
                        Hounsfield
                        Test Report
                    *********************

      Product Code ... PP
      Date ..........: 4.1.2002
      Batch Number ..: F
      Operator ......:
      Test Speed.....:     1.000{mm/min}

----------------------------------------------------------------------------------------------
         Max      Break      Ext @ Brk     1.000      2.000      3.000      4.000      5.000
        N          N           mm         N          N          N          N          N
----------------------------------------------------------------------------------------------
1      305.833    67.500      0.936      0.000      0.000      0.000      0.000      0.000
----------------------------------------------------------------------------------------------
```

Fig. A-5 Plot between load and extension using Fevibond without glow discharge for metal to polymer joint



```
            ********************
                Hounsfield
                Test Report
            *********************

Product Code ... PP
Date ..........: 4.1.2002
Batch Number ..: F
Operator ......:
Test Speed.....:    1.000{mm/min}

-----------------------------------------------------------------------------------------
       Max      Break     Ext @ Brk    1.000     2.000     3.000     4.000     5.000
       N        N         mm           N         N         N         N         N
-----------------------------------------------------------------------------------------
1    406.666   122.500     0.927      0.000     0.000     0.000     0.000     0.000
-----------------------------------------------------------------------------------------
```

Fig. A-6 Plot between load and extension using Fevibond with glow discharge for metal to polymer joint