Surface Modification of HDPE and PP by Mechanical Polishing and DC Glow Discharge and Their Adhesive Joining to Steel

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ABSTRACT: To improve the strengths of the adhesive joints of high density polyethylene (HDPE) and polypropylene (PP) to steel, the surfaces of HDPE and PP sheets have been treated by DC glow discharge to increase the polar component of surface energy significantly. Present study investigates the effect of mechanical polishing prior to surface modification of substrates of HDPE and PP sheets by exposure to DC glow discharge, on the surface energy and their adhesive joint strength to steel. The mechanical polishing has been carried out by abrading with 120, 220, 400, 600, 800, and 1000 grade emery paper of grit sizes 8.33, 4.54, 2.5, 1.67, 1.2, and 1 micron, respectively. The surface energy of a given surface has been evaluated by measuring contact angles of sessile drops of two test liquids of known surface tension components, such as deionized water and formamide. It is observed that 800-grade emery paper of grit size 1.2 micron has been found most effective in terms of their reduction in contact angles and enhancement of their surface energies. The change in surface energy due to surface modification has also been evaluated by measuring the surface energies of unpolished sheets exposed to DC glow discharge. The surface modification of the polymers by glow discharge for 120 s at a power level of 13 W decreases the contact angle more on mechanically polished specimens than that observed on unpolished sheets. Due to glow discharge treatment, the polar component of surface energy increases significantly in HDPE and PP, especially when they are mechanically polished (800 grade) prior to glow discharge. However, in case of the HDPE sheets, the effect of glow discharge on the polar component of surface energy is significantly higher compared to that for dispersion component of surface energy, whereas the polar component of surface energy of the PP sheet is lower than the dispersion component of surface energy. But in both the cases, mechanical polishing prior to glow discharge appears to affect the polar component of surface energy. Mechanical polishing of the HDPE and PP sheets by abrading with 800-grade emery paper prior to glow discharge treatment, increases the adhesive joint strengths over those observed in case of unpolished polymers exposed to glow

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discharge. However, the use of prior mechanical polishing increases the joint strength only by a little more than 10% compared to a five to seven times increase in strength observed as a consequence of exposure to glow discharge of as received samples. J Appl Polym Sci 80: 1140–1149, 2001

Key words: HDPE; PP; mechanical polishing; DC glow discharge; surface energy; adhesive joining; joint strength

INTRODUCTION

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 in many civil construction due to their superior properties like better corrosion resistance, high strength to weight ratio, relatively low cost and easy recycling.[1,2] Often these polymeric materials are adhesively bonded to primary metal structures. But unfortunately, these polymers exhibit insufficient adhesive bond strength due to their low surface energy. Thus, it is necessary to modify the surface of polymers to enhance their surface energy, which in turn, improves their adhesive bond strength.[3,4]

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 under low-pressure plasma or corona discharge under atmospheric pressure plasma.[5–7] Among different surface treatments, the low-pressure plasma treatment has been found most effective in respect of uniformity of surface modification and absence of chemical hazards.[8–10] Apart from surface modification by glow discharge, another simple but effective method to improve adhesion is by mechanical polishing of polymer surface, resulting in improvement of joint strength.[11,12]

In view of these observations, the present study investigates the effect of prior mechanical polishing on surface modification of HDPE and PP sheets by an optimum exposure to DC glow discharge.[13] The changes in the two components of surface energy, such as the polar and the dispersion components, have been evaluated by measuring contact angles of sessile drops on the unexposed sheets and on the sheets exposed to the DC glow discharge with and without mechanical polishing prior to exposure. Two liquids of known polar and dispersion components of surface energy have been used as test liquids for forming the sessile drops. Finally, the lap shear tensile strength of the adhesive joint of HDPE and PP with mild steel has been determined to compare the joint strength of the as-received unexposed polymer with that of surface-modified polymers.

EXPERIMENTAL

Materials

Commercial high-density polyethylene (HDPE) and polypropylene (PP) sheets of thickness 8 mm and mild steel sheets of thickness 1 mm were used for the preparation of adhesive lap joints of polymer to steel. The characteristics of the HDPE and PP sheets and chemical composition of the mild steel sheet are shown in Tables I and II, respectively. Two test liquids, such as deionized water and formamide, of known polar and dispersion components of surface tension, were used to determine the surface energies of HDPE and PP through measurement of their contact angles on the substrates of HDPE and PP by sessile drop method.[14,15] The known components of surface

Table I 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)
HDPE	8.0	965	60–82	27.5
PP	8.0	910	99–110	36

Sp. gravity and heat distortion temp. are as supplied by the manufacturer.

Table II Chemical Composition of the Mild Steel Sheet

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

Table III 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)
Deionized water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

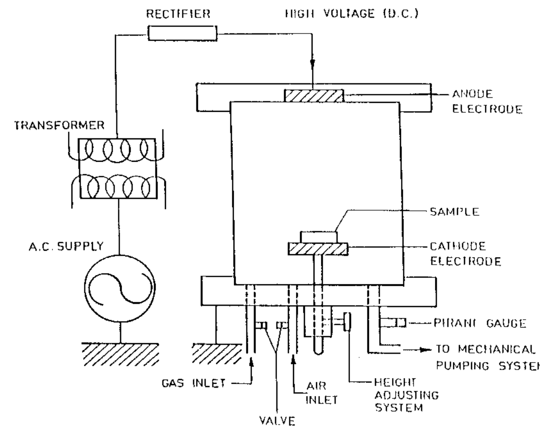

Figure 1 Schematic diagram of the DC glow discharge system used.

tension of the liquids are shown in Table III. The properties of a commercial epoxy adhesive (Araldite AY 105, Hardener HY 840), which was used to join the polymers with mild steel, are given in Table IV.

Surface Modification of the Substrates

Schematic diagram of the DC glow discharge setup, used for surface modification of HDPE and PP sheet, is shown in Figure 1. The setup 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 HDPE and PP sheets were cleaned by wiping with acetone 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 a 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 13 W for a period of 120 s at an electrode spacing of 110 mm. This is an optimum condition of surface modification of the HDPE and PP, which resulted in their highest adhesive joint strength with steel.[13] Prior to glow discharge exposure, some of the polymer substrates were mechanically polished by abrading on 120-, 220-, 400-, 600-, 800-, and 1000-grade emery papers of grit size 8.33, 4.54, 2.5, 1.67, 1.2, and 1 microns, respectively. Thus, two types of polymer substrates of HDPE and PP, with and without mechanical polishing under the above grades of emery paper, were prepared to study the effect of mechanical polishing on surface modification by DC glow discharge and to establish the optimum surface roughness condition in respect of their surface energies. The mild steel sheet was polished by abrading it on 400-grade emery paper, cleaned with acetone and joined with the surface-modified polymer with optimum roughness to determine the increase in adhesive joint strength, if any.

Estimation of Surface Energy

Contact angles of the deionized water and formamide sessile drops on the unexposed HDPE and

Table IV Details of Adhesive and Hardener Used

Epoxy Adhesive	Hardener	Composition (Adhesive: Hardener) Wt. Ratio	Mixing	Curing Schedule	Shear Strength of Adhesive (MPa)
Araldite AY 105 (Bisphenol A)	HY840 (PolyAmidoamine)	2 : 1	Manual	24 h at 25°C	7.4–9.8

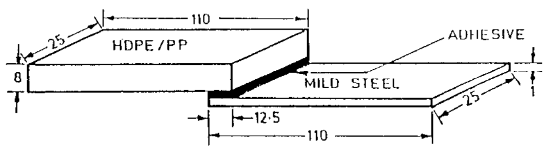

Figure 2 Schematic diagram of a lap shear tensile test specimen.

PP sheets with and without polishing and those surface modified by exposure under glow discharge, were measured. The geometry of sessile drop was studied at a magnification of ×12.8 under an optical stereo zoom microscope having a crossetched glass graticule fitted with an 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 measured using a goniometer, determined the contact angle with an accuracy of ±1°. The surface energies of the unexposed HDPE and PP sheets and the sheets exposed to glow discharge with and without mechanical polishing were estimated using the measured contact angles. The polar and dispersion component of surface energy of a polymer may be related to the contact angle and the surface energy of the test liquid[16–19] following the equation,

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

where, θ is the measured contact angle of the sessile drop of test liquid on the polymer surface 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 surface energy, γ_S, of the polymer surface. The γ_S^D and γ_S^P are estimated by solving the two equations set up for the measured contact angles of deionized water and formamide following eq. (1).

Adhesive Joint Preparation

Prior to preparation of an adhesive joint, degassing of the adhesive was carried out under a pressure of 1 Pa. 8-mm thick polymer sheet was used for preparation of the polymer to steel adhesive joint to ensure that the possibility of failure of the lap joint from either polymer or the mild steel is remote. The failure might take place either within the adhesive or at its interfaces with the polymer and steel. Thus, it provided 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 × 25 × 1 mm and 110 × 25 × 8 mm, respectively, by applying epoxy adhesive at an overlap length of 12.5 mm, according to DIN 23281 standard, as schematically shown in Figure 2. Any excess adhesive present at the interface was expelled out by rolling the joint at a load of 2 kg, which resulted in a joint having adhesive of thickness of about 0.2 mm. The shear tensile test was performed according to DIN 53283 standard, using Universal Testing Machine (Mohr and Federhaff AG), at a test speed of 5 mm/min.

RESULT AND DISCUSSION

Mechanical Polishing and Surface Energy

The contact angles of the formamide and deionized water on the unexposed polymers, HDPE and PP, and those exposed under glow discharge with and without prior polishing (1.2 microns) are shown in Figures 3 and 4, respectively. Figure 3 shows that the contact angles of formamide and deionized water on the unpolished HDPE exposed under glow discharge decreases to 41° and 56°, respectively, from 74° and 91°, as observed on the unpolished surface of HDPE not exposed under glow discharge. However, mechanical polishing of the HDPE sheet prior to exposure under glow

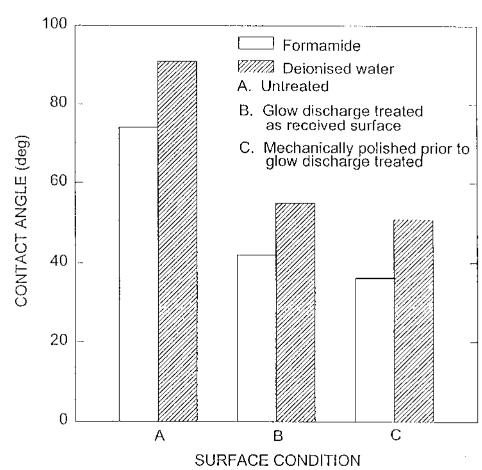

Figure 3 Variation of contact angle of a sessile drop of formamide and deionized water on different surface conditions of HDPE at a glow discharge power of 13-W and exposure time of 120 s.

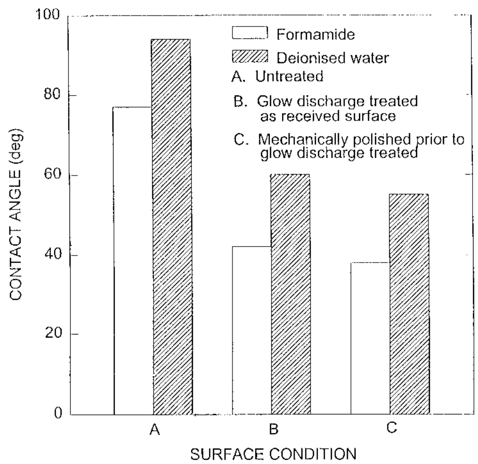

Figure 4 Variation of contact angle of a sessile drop of formamide and deionized water on different surface conditions of PP at a glow discharge power of 13-W and exposure time of 120 s.

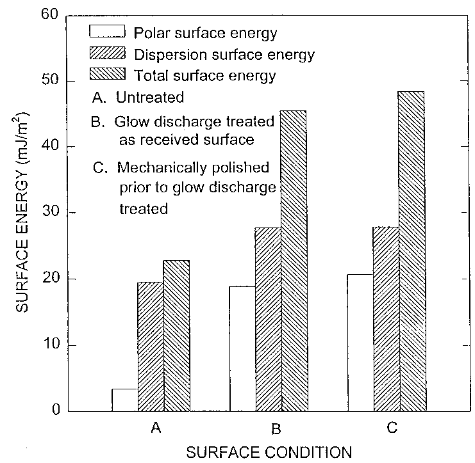

Figure 6 Variation of total surface energy and its two components on different surface conditions of PP at a glow discharge power of 13-W and exposure time of 120 s.

discharge decreases the contact angles further to 36° and 51° for the test liquids of formamide and deionized water, respectively (Fig. 3). In the case of the PP sheet, the exposure under glow discharge decreases (Fig. 4) the contact angles to 42° and 60° from 77° and 94°, as observed on surface not exposed under glow discharge, for the test liquids of formamide and deionized water, respectively. The glow discharge treatment on the mechanically polished PP sheets also decreases the contact angle further to 39° and 56° for formamide and deionized water, respectively.

The polar and the dispersion components of surface energies and the total for the as-received unexposed HDPE and PP sheets and those exposed to glow discharge without and with prior mechanical polishing are shown in Figures 5 and 6, respectively. The figures reveal that the polar component of surface energy of both the HDPE and PP increases significantly due to exposure under glow discharge compared to that observed for the surfaces of the polymers not exposed under glow discharge, and it marginally increases further with the application of mechanical polishing prior to their exposure under glow discharge.

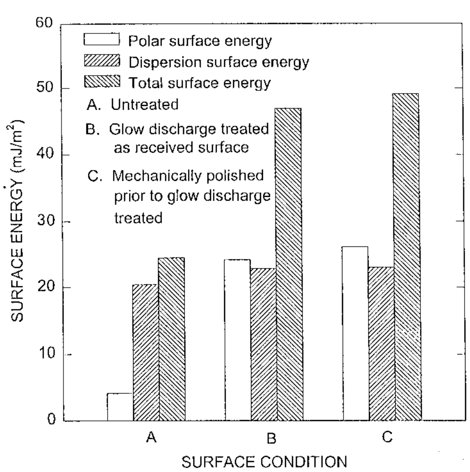

Figure 5 Variation of total surface energy and its two components on different surface conditions of HDPE at a glow discharge power of 13-W and exposure time of 120 s.

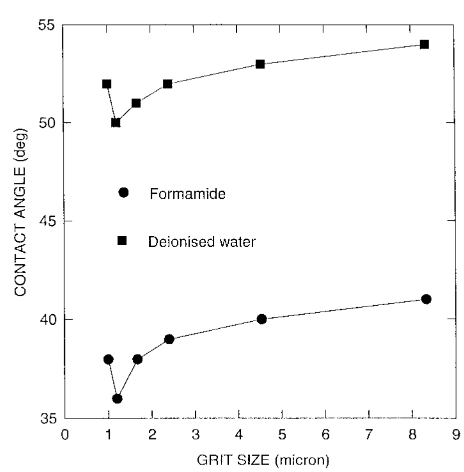

Figure 7 Variation of contact angle of sessile drop of formamide and deionized water on a mechanically polished HDPE sheet prior to glow discharge at 13-W power and 120 s of exposure time.

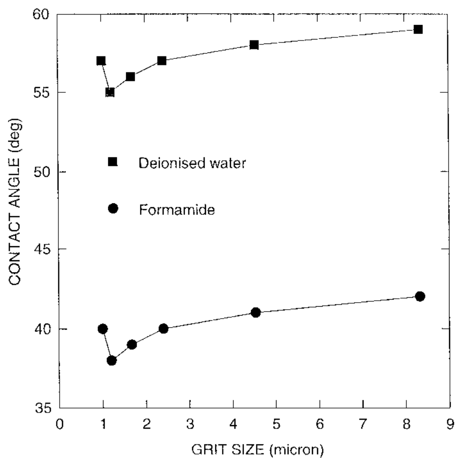

Figure 8 Variation of contact angle of sessile drop of formamide and deionized water on a mechanically polished PP sheet prior to glow discharge at 13-W power and 120 s of exposure time.

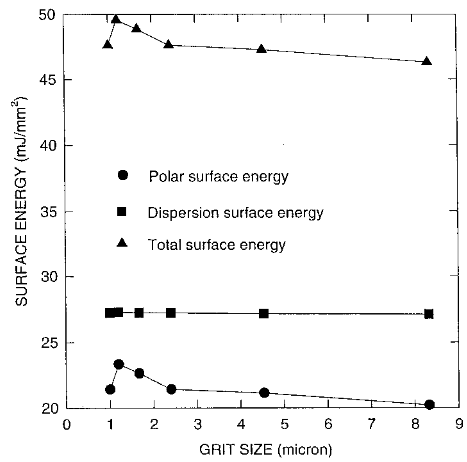

Figure 10 Variation of total surface energy and its two components on a mechanically polished PP sheet prior to glow discharge at 13-W power and 120 s of exposure time.

However, in the case of the HDPE sheet, the change in polar component of surface energy on exposure under glow discharge with or without prior mechanical polishing is significantly higher compared to the marginal change in the dispersion component of surface energy. In the case of the PP sheet, the dispersion component of surface energy (Fig. 6) changes moderately with the exposure under glow discharge, and the polar component of surface energy is lower than its dispersion component. However, in both the cases of HDPE and PP, mechanical polishing prior to exposure under glow discharge appears to affect primarily the polar component of surface energy. Due to significant enhancement of polar component of surface energy of the polymers, their total surface energy increases significantly when exposed under glow discharge, and it increases further when polished prior to exposure under glow discharge as shown in Figs. 5 and 6 for HDPE and PP sheets, respectively. However, the decrease in contact angle due to mechanical polishing prior to exposure under glow discharge depends on the level of surface roughness of the polymers, as it has been observed that contact angles attain a minimum when the polymers are polished using an emery paper of a grit size of 1.2 microns, and then it increases with further enhancement of

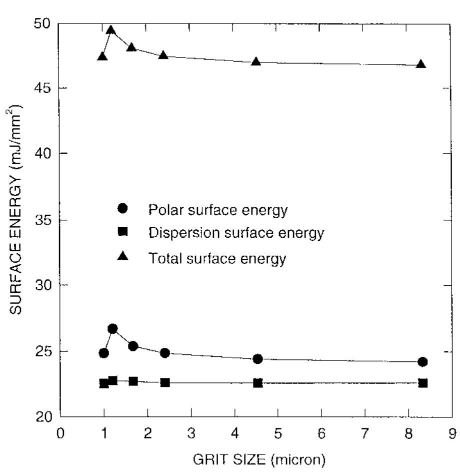

Figure 9 Variation of total surface energy and its two components on a mechanically polished HDPE sheet prior to glow discharge at 13-W power and 120 s of exposure time.

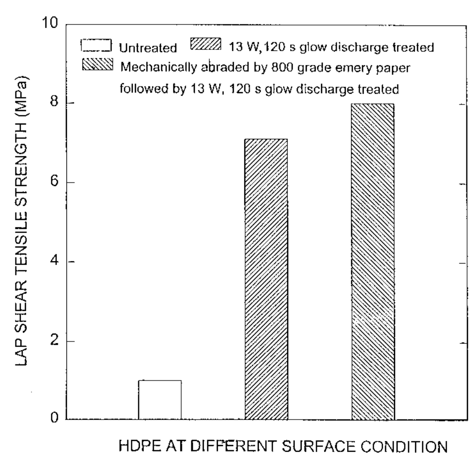

Figure 11 At an optimum surface roughness of HDPE the influence of effective glow discharge treatment on HDPE on lap shear tensile strength.

surface roughness, as shown in Figures 7 and 8 for the HDPE and PP sheets, respectively. Consequently, the surface energy of the polymers is observed to attain maximum at the above surface roughness as shown in Figures 9 and 10, respectively, for the HDPE and PP sheets.

Surface Treatment and Strength of Adhesive Joint to Steel

The lap shear tensile strengths of the adhesive joints of as-received unexposed HDPE and PP sheets and those exposed to glow discharge with or without mechanical polishing with mild steel are shown in Figures 11 and 12, respectively. Both the figures depict that exposure under glow discharge of the as-received polymer surfaces enhances the adhesive joint strength by about five to seven times compared to that observed in the case of the adhesive joint of the as-received unexposed polymer to mild steel. Mechanical polishing of HDPE and PP sheets prior to glow discharge increases their adhesive joint strength with steel over that observed in the case of similar adhesive joints of the unpolished but glow discharge-treated polymers. However, the joint strength increases only by a little more than 10% due to mechanical polishing. Both the adhesive joints of the as-received unexposed HDPE and PP sheets

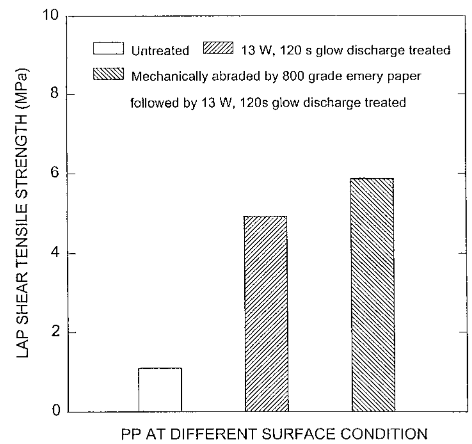

Figure 12 At an optimum surface roughness of PP the influence of the effective glow discharge treatment on PP on lap shear tensile strength.

with steel have been generally found to fail from the adhesive to polymer interface. However, when HDPE surface has been modified by exposure under glow discharge without prior mechanical polishing, the mode of failure is complex, as the failure takes place in the polymer–adhesive interface, cohesively in the adhesive and in the steel–adhesive interface. The different observed modes of failures of the HDPE and PP to mild steel

Table V Mode of Failure of Polymer—Steel Adhesive Joint

		Mode of Failure (Mean Relative Fraction of the Area of Fracture)		
Joined Materials	Treatment of Polymer	Failure at Polymer Adhesive Interface (A)	Failure within the Adhesive (B)	Failure at Mild Steel Adhesive Interface (C)
HDPE—mild steel	As received and unexposed	100	0	0
	Exposed under glow ischarge (13 W, 120 s)	13.8	18.18	68.64
	Mechanically polished (1.2 micron) and glow discharge exposed (13 W, 120 s)	0	0	100
PP—mild steel	As received and unexposed	100	0	0
	Exposed under glow discharge (13 W, 120 s)	100	0	0
	Mechanically polished (1.2 micron) and glow discharge exposed (13 W, 120 s)	100	0	0

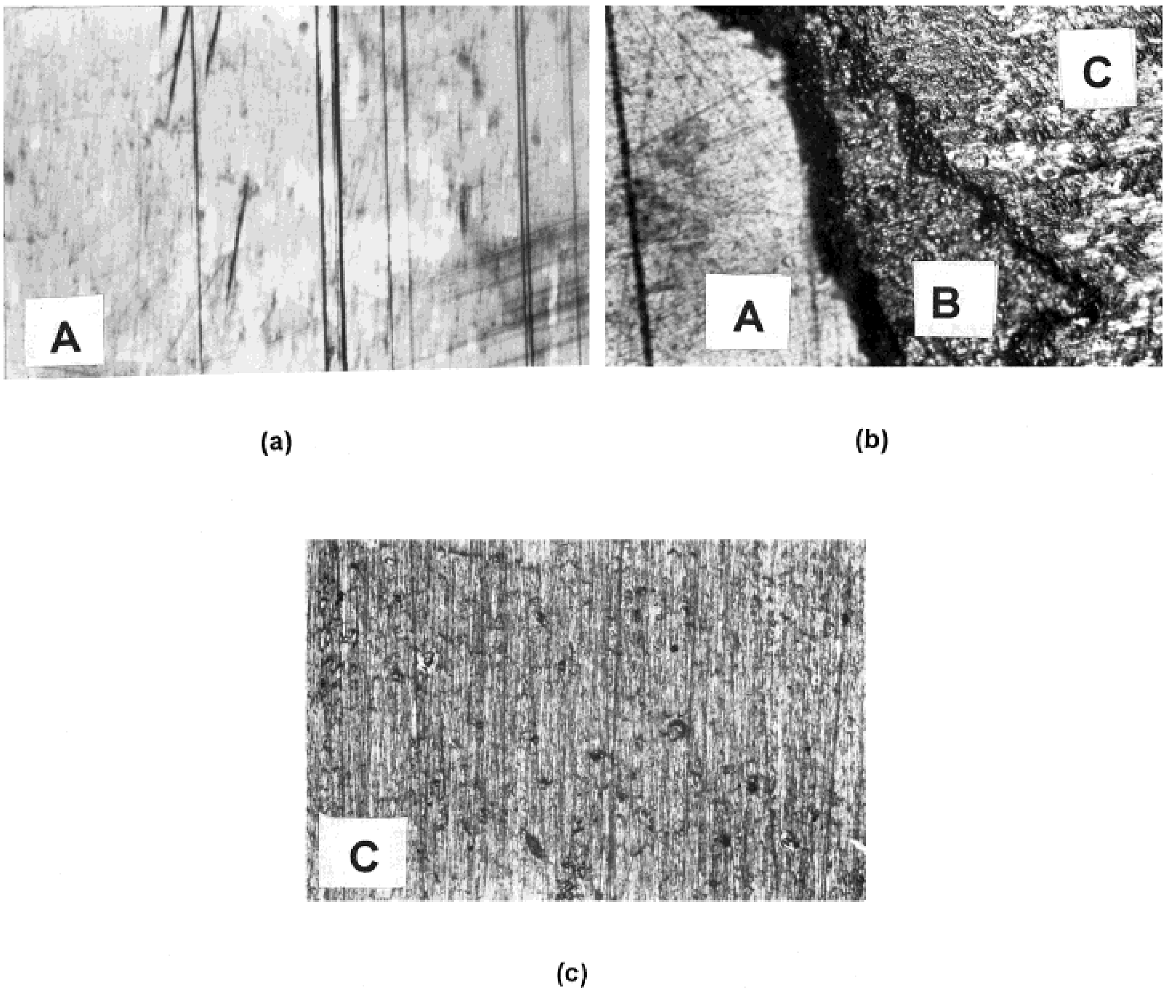

Figure 13 Optical micrograph of HDPE fracture surfaces of HDPE–steel adhesive joints (magnification ×25) (a) showing the polymer–adhesive interface failure (A) in as-received and unexposed polymer joined to mild steel, (b) showing complex mode of failure through the polymer–adhesive interface (A), adhesive cohesively (B) and through the adhesive–steel interface (C) in glow discharge-exposed polymer joined to mild steel, and (c) showing the steel–adhesive interface (C) in mechanically polished polymer prior to exposure under glow discharge joined to mild steel.

adhesive joints are listed in Table V, and are shown in Figures 13 and 14, respectively, by optical micrographs where A, B, and C indicates regions of polymer–adhesive interface failure, cohesive failure of the adhesive, and mild steel–adhesive interface failure, respectively.

The surface energy increases when a polymer surface is exposed under glow discharge, as is evident from lowering of the contact angle of the test liquids. Various authors have reported that contact angle of deionized water on polyethylene (HDPE/LDPE) and PP surfaces decreases significantly due to plasma treatment of the substrates.[10,20,21] It is also observed that the contact angle decreases with increasing the surface roughness as the rough surface develops capillarity.[22] The present investigation shows that mechanical polishing of the polymer surface prior to exposure under glow discharge leads to a comparatively larger decrease in the contact angle in comparison to that observed on an unpolished polymer exposed under glow discharge. During surface modification of polymer by low-pressure plasma, the polar component of the 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] It is observed[8]

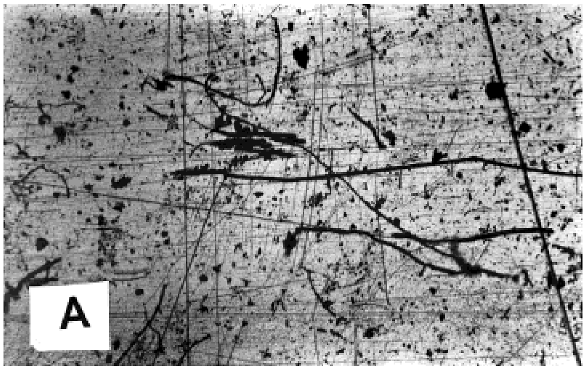

Figure 14 Optical micrograph of a typical PP fracture surface of PP–steel adhesive joints (magnification ×25) showing polymer–adhesive interface failure (A).

that the polar component of the surface energy of the polymer improves significantly with a short exposure to plasma. However, the dispersion component of surface energy remains almost unaffected. It is also reported[23] that polar component of the surface energy increases significantly when plasma treatment is carried out at 750 V for 450 s. The present investigation shows (Figs. 5 and 6) that the polar component of the surface energy of both the HDPE and PP sheets increases significantly upon exposure to glow discharge, and it enhances further due to application of mechanical polishing. Exposure of polymer under glow discharge primarily increases the polar component of surface energy, and mechanical polishing may be contributing further by increasing the surface area per unit flat area on the surface. Because the dispersion component of the surface energy remains more or less unaffected by mechanical polishing, the increase in the effective surface area may not be as significant. It may be possible that the strain energy introduced by mechanical polishing to the polymer surface has helped the plasma to create more polar groups on the surface during exposure under DC glow discharge. Niem et al.[12] have shown that adhesive joint strength of PMMA adherends increases in the mechanically abraded sheet. It has been reported that under nonabraded condition, the joint strength is 1100 N, and it increases by about 30% up to 1501 N, using a 1.20-micron abraded sheet. This may be attributed to an increase of the surface area due to surface roughness.

CONCLUSION

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

1. Exposure of HDPE and PP sheets under glow discharge for 120 s at a power level of 13 W, reduces the contact angle of formamide and deionized water significantly, and mechanical polishing prior to glow discharge reduces it further for both the HDPE and PP sheets.
2. Prior mechanical polishing of the HDPE and PP sheets and exposure under glow discharge shows higher polar and total surface energies over those observed for both the as-received and unexposed HDPE and PP sheets and those exposed only to glow discharge without polishing. Mechanical polishing primarily affects the polar component of the surface energy, but the dispersion component of surface energy remains more or less unaffected.
3. Mechanical polishing of HDPE and PP sheets prior to glow discharge exposure increases the adhesive joint strength over that obtained in joints with either the as-received and unexposed polymers or the polymers exposed only to glow discharge without prior mechanical polishing.

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