Adhesion studies of the atmospheric pressure plasma treated polypropylene fabric coated with polyurethane

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ABSTRACT : *The aim of this study was to analyse the effect of plasma treatment on adhesion properties of polyurethane (PU) coated polypropylene fabric. The effect of the plasma parameters vis. time and power on adhesion improvement was examined. The force required to separate the coating from the fabric was measured as per IS 7016 part 5 standard test method. Significant improvement in the adhesion of the plasma treated sample was found compared to untreated samples. Adhesion strength showed significant improvement with increase in plasma treatment time and power. Changes in surface morphology were analysed using scanning electron microscope. Surface wettability was studied by contact angle and surface energy measurement. Slight reduction tensile properties was observed with increase in plasma power.*

KEYWORDS *Adhesion improvement, coating, Plasma treatment, polypropylene, Polyurethane.*

I. INTRODUCTION

Synthetic fibres have revolutionized the textile industry since their initial commercialization in 1940. Synthetic fibres such as polypropylene (PP), polyester (PET), polyamide (PA) etc. are widely used in technical textiles and home furnishings due to their good physical and chemical properties. The demand of these fibres increases greatly for high performance applications such as smart textiles, technical textiles, operation clothing etc. and more recently, for their potential applications in electronic textiles [1,2]. However, these fibres are hydrophobic in nature due to the lack of polar functional groups. The hydrophobic nature of such fabrics limits their application. Textile coatings are widely used in everyday life including above mentioned areas. The purpose of the coating is to provide its carrier material with specific functional properties for suitable application. The surface of the synthetic fibre is generally inert, making the fibre difficult to wet and hard to chemically bond to coating material, as a result the adhesion between the fibre and coating material is inferior [3,4]. Adhesion is fundamentally a surface property, often governed by a layer of molecular dimensions, which necessarily required for coating, bonding and printing of synthetic textiles. The surface smoothness and low surface energy of hydrophobic polymeric materials results in intrinsically poor adhesion.

In order to improve adhesion to coating fibres are usually subjected to controlled surface treatments. The main purpose of surface modification of fibres used as reinforcements in composite materials is to modify the chemical and physical structures of the surface layers, tailoring fibre-matrix bond strength, but without influencing their bulk mechanical properties. Chemical surface treatments of fibres have been widely used in industry for a long time. However, chemical modification may have some disadvantages. For example when fibres are oxidized in concentrated nitric acid, the equipment used must have good corrosion resistance and the acid adsorbed on the fibre surface must be properly removed. This is time consuming and, in most cases, is accompanied by a decrease in fibre strength. Moreover, these conventional treatments can also lead to environmental pollution. Therefore, it is important to explore other techniques. Surface modification of textile fibres by cold plasma is simple and does not require the use of water and chemicals, resulting in a more economical and ecological process. Due to enormous advantage of plasma processes it is becoming increasingly popular [5-11].

The aim of this study was to improve the surface properties of the polypropylene (PP) fabric by atmospheric pressure plasma generated form helium gas for better adhesion of PU polymer to surface of PP fabric.

II. Materials and Methods

2.1. Materials

A woven PP tape × tape fabric with an area weight of 130 g/m^2 is used in this study. PP tape× tape fabric was supplied by Felxituff Limited, India. Polyurethane (commercial name: TUBICOAT MP SP) was supplied by CHT India. Helium gas (He) with 99.995% purity was procured from INOX air products, India.

2.2 Plasma Treatment of PP fabric

Plasma treatment of PP was carried out on atmospheric pressure plasma reactor, PLATEX-600 (make GRINP S.R.L., Italy). The schematic of the plasma reactor is shown elsewhere [12]. The system operates in continuous mode where online treatment of fabric is possible. The length of plasma zone (total length of electrodes in the direction of fabric movement) is 12 cm and width is 55 cm. The minimal possible gap of 1 mm was kept in-between the electrodes during the plasma treatment of the PP fabric. Plasma was generated from helium gas. Gas was fed to the electrode system where electrical power was applied to the electrodes to generate plasma.
Two sets of experiments were carried out to capture the data on exposure time and power parameters of plasma. In experimental set I plasma power was kept constant at 1.5kW and plasma exposure time was varied to 15S, 30S and 45S. The discharge power for plasma generation was kept at 1.5kW, 2.5kW and 3.5kW in experimental set II keeping the plasma exposure time constant at 15S. Helium gas flow was maintained at 5 lit/min throughout experiments.

2.3 Application of PU coating on the PP fabric:

2.3.1Formation of PU foam

100gm of Tubicoat MP SP was taken in 500ml of plastic beaker and mixed with high speed blender till volume of the coating chemical get increased by 4 times of the original volume. The initial density of the PU was 1gm/cm^3 which was reduced after high speed blending to 0.25gm/cm^3.

2.3.2 Coating process

Above light weight PU foam was applied on the plasma treated PP fabric with knife over roller coating method using hand coating machine. The knife moves over the fabric to apply the uniform coating with predetermined thickness. 3mm thick coating was applied on all samples.
After application of PU coating, samples were~~as~~ dried at 80°C for 10min. After drying the coated samples were~~as~~ cursed at 4bar pressure with 2nip using padding mangle, and finally curing was carried out at 130°C for 10min. Similarly untreated PP sample was also coated with PU to study the effect of plasma treatment for adhesion improvement.

III. Characterization techniques

3.1 Adhesion strength test

The adhesion strengths of untreated and plasma treated coated fabrics were determined by a peel bond strength test. The peel bond strength of coated samples was measured according to the IS 7016 part 5- 2011 test standard with a Tinius olsen, peel bond tester. Five different measurements were performed and average value is considered as bonding strength of the coated fabric.

3.2 Contact angle and surface energy Measurement

Easy Drop standard drop shape analysis system (KRUSS GmbH, Hamburg, Germany) equipped with high-speed camera IEEE1394b interface was used for the measurement of the contact angle on PP fabrics. Four different test liquids, namely water (W), Glycerol (G), Formamide (F) and ethylene glycol (E) were used to measure the static contact angle on samples treated under different plasma conditions. Fowkes question is used to calculate the surface energy of the different samples.

3.3 SEM analysis

Surface topographical modifications in the PP samples before and after plasma treatment were investigated by scanning electron microscopy (SEM) on JEOL SEM model JSM 5400 (Tokyo, Japan).

3.4 Mechanical properties

Tensile strength of the untreated and plasma treated samples were carried out on pyramid tensile testing machine model Tinius olsen H50KL Aimil. ASTM D 5035 -2015 standard test method was used. Average of the five test specimens was considered as the tensile strength of the fabric.

IV. Results and Discussion

4.1 Adhesion strength

Adhesion strength was measured as force required to separate the coating layer form the fabric. The peel off strength of the untreated and plasma treated PP coated samples is given in Fig. 1. The adhesion bond strength of plasma treated coated samples showed more than five times increase compared to the untreated coated sample. As can be seen from Fig. 1, increasing the plasma exposure time and power enhanced the peel bond strength. As the plasma treatment time was increased ~~from~~ 15 sec., 30 sec. and ~~to~~ 45 sec, the peel bond strength increased by 500%, 530% and 565% at a plasma power of 1.5kW respectively. The highest peel bond strength value was obtained at a plasma power of 1.5kW and plasma time of 45 sec. it can be seen from Fig. 1, that the plasma treatment time is more effective in improving the adhesion than the plasma power. The results are in agreement with recent studies showing that the degree of plasma modification depended on the plasma exposure time and discharge power [13, 14]. Increase in adhesion strength may be attributed to surface roughness and polar groups created by plasma treatment.

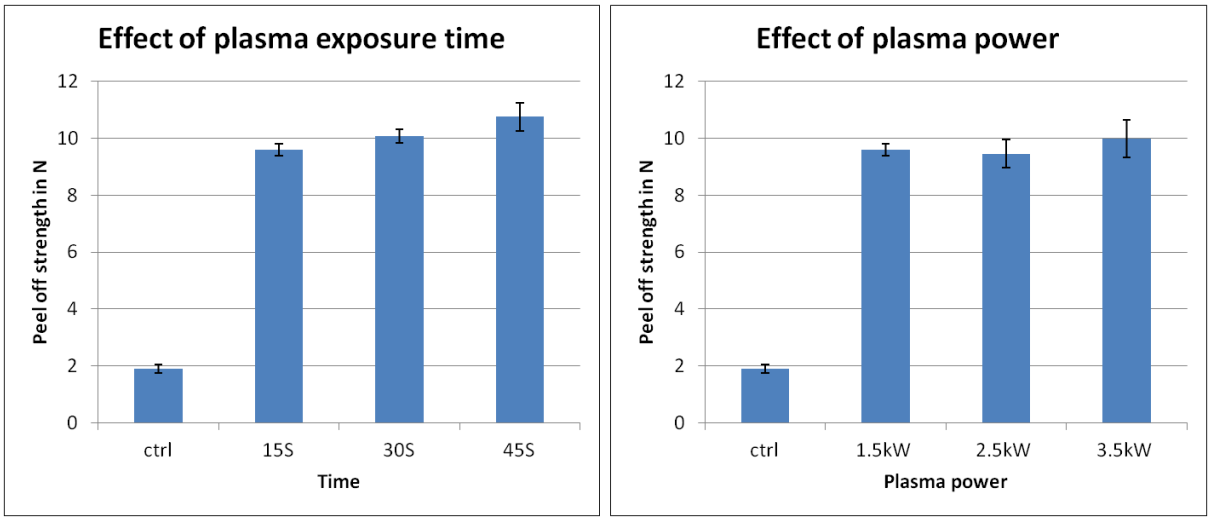

Figure 1. Effect of plasma treatment on the adhesion properties of PP coated samples

4.2 Contact angle and surface energy measurement

Wettability behaviour of a material can be determined from the contact angle values. A decrease in the contact angle indicates an increase in wettability [15, 16]. Materials that have over ~~a~~ 90 degree contact angle are considered as hydrophobic and those that have ~~a~~ less than 90 degree contact angle are hydrophilic. The contact angle values with different liquids for plasma treated and untreated samples are given in the Table 1.

Table 1. Contact angle and surface energy of the untreated and plasma treated samples.

samples	Contact Angle (°) with				Surface Energy (mJ/m^2)
	Water	Glycerol	Formamide	Ethylene Glycol	
Ctrl	85.5	81.5	72.2	63.9	23.32
Effect of plasma exposure time					
1.5kW 15S	72.6	70.8	55.1	48.5	32.44
1.5kW 30S	72.9	69.2	52.8	48.1	33.11
1.5kW 45S	73.1	71.3	65.1	47.4	31.17
Effect of Plasma power					
1.5kW 15S	72.6	70.8	55.1	48.5	32.44
2.5kW 15S	76.3	72.1	60.1	54.7	29.83
3.5kW 15S	71.6	70.1	58.4	48.4	32.46

It can be seen from Table 1 that after plasma treatment the contact angle values of all the samples with all four liquids are reduced compared to untreated PP sample. Contact angle of each sample was measured with four different liquids to calculate the surface energy (SE).

Solid surface tension is an important thermodynamic quantity governing many technological processes. However, because of the absence of surface mobility, a solid phase is very different from a liquid phase; hence, one cannot measure the surface tension of a solid phase directly as in the case of liquid phase. Among the different indirect approaches to determine solid surface tensions, contact angle is believed to be the simplest and hence widely used approach [17,18].

Table 2. Surface Tension Parameters for selected Liquids at 20°C in mJ/m^2

Liquids	Surface Tension Parameters				
	γ_l	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.8	21.8	51	25.5	25.5
Glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
Ethylene Glycol	48	29	19	1.92	47

Choice of a liquid for SE measurement is a crucial thing. The test liquids are so chosen that their polar and disperse components of ~~a liquid~~ surface tension are known to calculate the SE components of the solid by measuring contact angles. Water is a common chose to measure contact angle since its properties are well established.

To calculate the surface free energy of the substrate a set of minimum three liquids of known polar and disperse components are required. To minimize the error involved, we have used four liquids. Surface tension parameters for selected liquids are given in Table 2.
Fowkes approximation is used to calculate the SE. The equation to calculate surface free energy by using Fowkes approximation [19, 20] is as follows:

$$\left[\frac{1+\cos\theta}{2}\right] \times \left[\frac{\gamma_l}{\sqrt{\gamma_l^d}}\right] = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \qquad (1)$$

The equation is of the form

$$\gamma\ (LHS) = mX(RHS) + C \qquad (2)$$

where value of LHS can be obtained by calculating θ for the liquid used. Value of γ_l and γ_l^d can be obtained from Table 2. Similarly, RHS can be calculated by using polar and disperse components of liquid used. Surface energy of the untreated and plasma treated samples is calculated by Fowkes equation and ~~is~~ given in table 1. It can be seen from the table that SE of the untreated samples is 23.32 mJ/m^2 which is increased up to 33.11 mJ/m^2 after plasma treatment. This suggests that after plasma treatment the wettability of PP samples increased.

4.3 Surface morphological analysis by SEM

Figure 2 shows SEM images of untreated and plasma treated polypropylene tape samples. Morphological changes on the surface after helium plasma treatment can be observed. The untreated PP tape has smooth and clean surface, while plasma treated PP tape show rougher surfaces. The surface roughness increased with the increase in plasma power. Plasma induced roughening was observed on the polypropylene surface, as also reported in previous studies [21, 22].

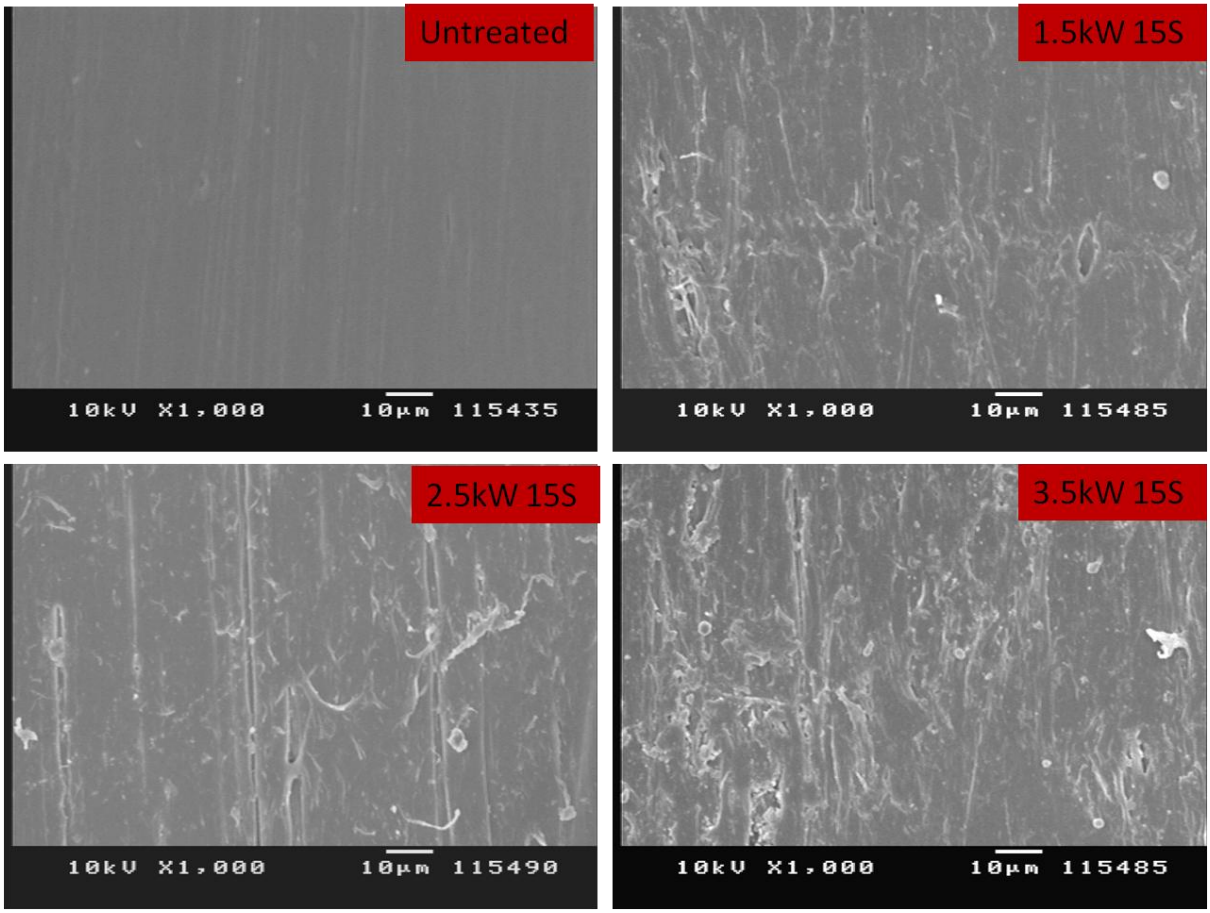

Figure 2 SEM images of untreated and plasma treated PP tape fabric before coating.

It is clear that helium plasma treatment etched the surfaces. Rough surface results in increased in surface area. Morphological alteration of the PP surface might lead to improved mechanical adhesion due to the roughening effect and larger surface area.

Figure 3 shows the cross sectional SEM images of the untreated coated (Fig. 3~~8~~A) and plasma treated coated (Fig. 3~~8~~B) samples. It can be seen that PU polymer is well adhere to plasma treated PP fabric as compared to untreated one. These results are well in agreement with results of contact angle and surface energy. As the contact angle reduces the wetteing and spreading properties of the surface increases. This improved wettabilty results in better anchoring of the PU polymer with PP surface, hence result in improved adhesion strength.

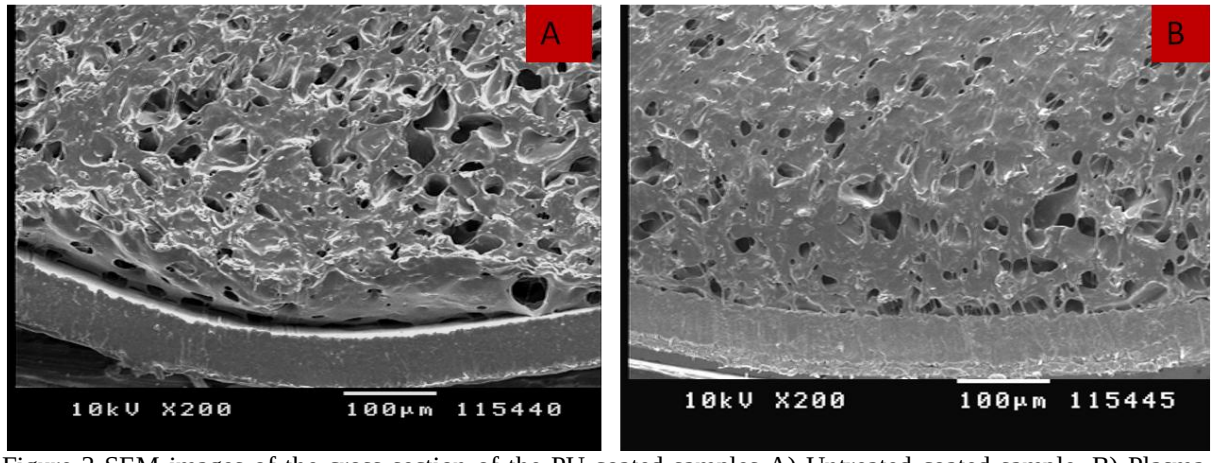

Figure 3 SEM images of the cross section of the PU coated samples A) Untreated coated sample, B) Plasma treated coated sample.

After the peeling test, the remaining adhesive on the fabric surface can be seen in the SEM micrographs in Fig. 4 There is more remaining adhesive on the plasma treated surfaces than that of untreated surfaces, as also revealed in previous studies [23]. PU adhesive is mainly attached to the surface of plasma treated PP filling the spaces between fibres.

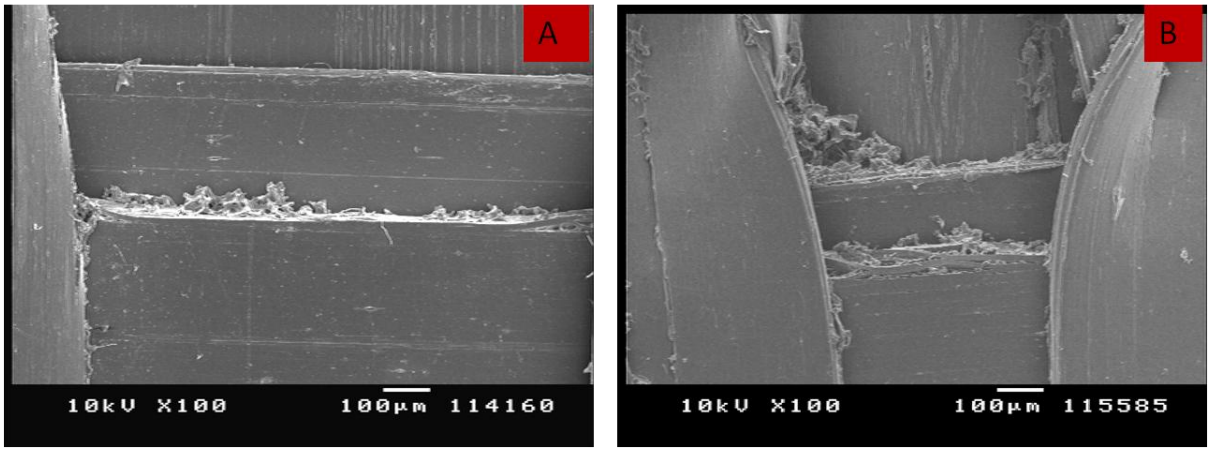

Figure 4 SEM images of remained adhesives on the surface after peel off A) untreated, B) Plasma treated.

4.4 Mechanical properties

The effect of plasma exposure time and discharge power on the tensile properties of PP fabric is evaluated in warp direction and depicted in Fig. 5. The initial tensile strength of untreated PP fabric was 28.3 N/mm. For lower discharge power and time of 1.5kW 15sec, tensile strength of PP fabric was 27.58 N/mm, showing hardly any effect on tensile strength. However, further increase in the discharge powers to 2.5kW and 3.5kW has yielded tensile strength values of 23.79 and 19.8 N/mm respectively. It was observed that longer plasma exposure time and higher discharge powers considerably deteriorate the tensile properties of the PP sample during plasma treatment. The deterioration in tensile properties of PP fabric may be attributed to formation of weak spots on fabric surface due excessive etching process.

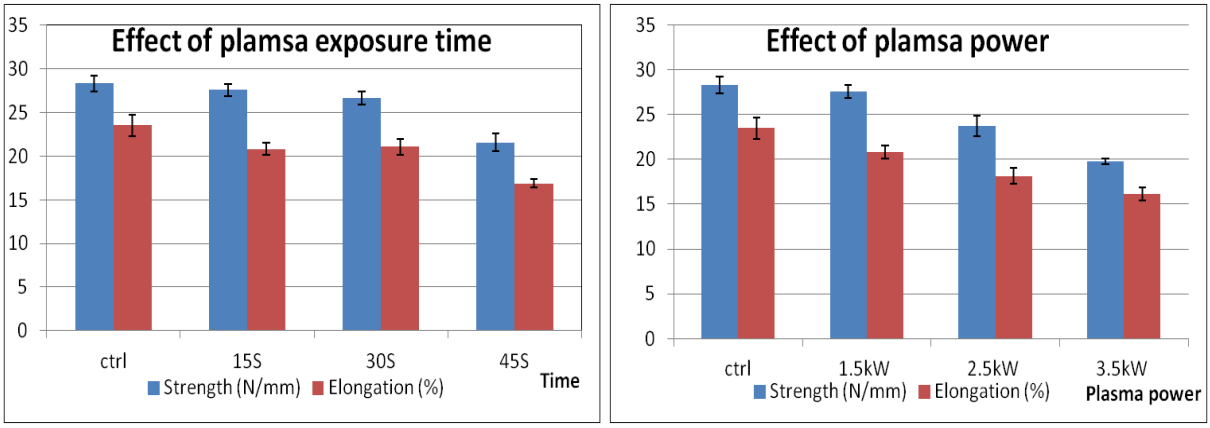

Figure 5 Tensile strength of the PP fabric, effect of plasma treatment.

V. Conclusions

Plasma treatment of PP tape by tape fabric was carried out at atmospheric pressure using helium gas. SEM images of the plasma treated PP fabric showed the surface roughness and results in increased in surface area. Plasma treated PP fabric was coated with PU polymer and adhesion studies was carried out by peel bond test. It was observed that with increase in plasma exposure time there is significant improvement in peel bond strength. Almost 550% increase in peel bond strength was observed compared to untreated fabric. Contact angle of plasma treated sample is decreased significantly as compared to untreated sample making the sample more wettable. Surface energy of the plasma treated sample was increased after plasma treatment. Tensile strength of the PP was decreased at higher power and for longer plasma exposure time. Plasma treatment of 1.5kW for 15 sec gives the excellent improvement in adhesion strength without affecting mechanical properties.

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