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Comparative study of surface morphology and spectroscopic analysis for plasma and ammonium persulphate treated polyethylene film for water based ink printing

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ABSTRACT

Polyethylene, Specially the LDPE is one of the most widely used thermoplastic in packaging industries, due to its low cost, broad range of properties like excellent moisture barrier and chemical resistance which are need for food packaging sectors. As mentioned above LDPE is most widely used plastic for packaging film applications but the major disadvantage is that the surface of the LDPE film is smooth and non-polar also shows the lack of chemical functionality which is a requirement for adhesive bonding, hence surface preparation/modification become necessary. Often which adhesion properties increase of all the available methods to modify the polymer surface for enhancing adhesion properties, here in this study we have used plasma treatment and aqueous solution of Fe3+ ion salt with ammonium persulphate treatment to modify surface of LDPE film. The modification in surface due to the treatments were correlated by means of Fourier transformed infrared spectroscopy (FTIR) to determine the presence of polar species such as carbonyl, carboxyl and hydroxyl groups etc. The improvement in ink adhesion, both water based and solvent based inks was studied by standard Scotch tape adhesion test. Furthermore Surface property and Surface morphology was characterized by contact angle measurement and Scanning Electron Microscope (SEM). Surface energy and surface roughness can be directly correlated to the improvement in surface-related properties.

KEYWORDS

Fe3+ ion salt with ammonium persulphate Etching;
Plasma treatment;
Printability.

INTRODUCTION

Major products of packaging industry require aesthetic value which makes printing an essential part of packaging industry. In conventional printing i.e. solvent based process the rate at which the solvent evaporates is very high releasing a volatile organic compound (VOC) which poses a serious threat to our environment. This has increased the demand for a substitute like water based inks. Packaging Industry demands mostly LDPE because of its high specific modulus, strength, abundant availability, good process ability, low energy consumption, resistance to chemicals and low cost. However LDPE

is Smooth & nonpolar in nature, due to which it exhibits poor adhesion property hence printing of LDPE surface is poor[2]. Surface topography and the presence of polar groups on the surface play a crucial role for obtaining good adhesion. Change in the chemical composition and morphology of the surface may enhance the adhesion property[5-6]. A number of methods have been utilized to modify the LDPE surface such as plasma treatment[16],corona treatment[12] & chemical etching[18]. In continuation of the investigation we repeat here the results of aqueous solution of Fe3+ ion salt with ammonium persulphate etching and plasma treatment of our own attempts to modify LDPE surface. The spectroscopic analysis ATR-FTIR has characterized polar groups. The printability of LDPE film with water based and solvent based ink was determined by Scotch tape test. The mechanism of improvement of the above mentioned surface related property of LDPE film is discussed.

EXPERIMENTAL

Materials

1. LDPE grade (24 FS040) of Reliance was blown into smooth films by usual extrusion film blowing technique. It has Melt flow index 4.0 gm/10 min, Density 0.922gm/cc. high slip grade.
2. Fe $(NO_3)_3$ from S.D. Fine Chemical, India.
3. Ammonium persulphate from MERCK India Ltd.
4. Inks were procured from Micro Inks Ltd.

Preparation of blown films

LDPE grade (24 FS040) Reliance was blown into smooth films by extruding through a 1 in. centering vertical die using a Boolani blown film extrusion, blown, cooled, and collapsed to films of approximately 3-in.width.

Surface modifications

Plasma treatment

1. The films were cleaned with acetone in an ultrasonic bath for 6 min and then dried in air. LDPE films were partially crystalline in nature.
2. A typical bell jar type plasma reactor having a height of 30 cm and a diameter of 30 cm was used. The two electrodes were capacitive coupled to the RF source capable of giving power output up to 100 W.
3. Various ports were fitted on the base plate for gas and monomer inlet. Pirani gauge was fitted onto the top plate. To confine the glow discharge to the specific volume, the magnetron was mounted on the base plate. Because of magnetron, the plasma confined to a volume of 500 cm^3 and the maximum sample that can be uniformly treated in our plasma chamber is 10 cm × 10 cm. However, LDPE films of size 8 cm × 8 cm were used in the present work.
4. The working pressure was adjusted to 0.2 mbar and gas flow rate to 15 SCCM.

Aqueous solution of Fe3+ Ion salt with ammonium persulfate treatment

1. LDPE film was cut into sizes of 10 ×5 cm and the film samples were washed with hydrochloric acid (HCl), Acetone, and distilled water and finely dried in oven at about 60°C.
2. Then the dried films were dipped in the aqueous solution of ammonium persulfate and $Fe(NO_3)_3$ at a desired temperature for a different periods of immersion placed in a temperature bath.
3. After the treatment, the film was dipped in deionized water, then washed and dried at 50°C.

CHARACTERIZATION

Weight and thickness measurement

The effect on the surface treatment on weight and thickness of the LDPE films were measured with the help of analytical balance and thickness gauge respectively. The pre and post condition of the films were noted down to analyze the effect of surface treatment

Dynamic contact angle measurement

A Cahn Dynamic Contact Angle Analyzer (Model DCA312) from Cahn Instrument was used for all Dynamic Contact Angle measurements. The LDPE film sample was glued to both sides of a thin glass slide measuring 24 x 30 mm with the treated side facing outside used as the sample element. Advancing and receding contact angles of the sample ele-

ment were determined by the dynamic contact angle analyzer as the sample element went through the immersion and emersion cycles in water. The advancing and receding contact angles from two immersions cycle were averaged and reported.

SEM analysis

Surface morphology of the corona treated as well as chromic acid etched & unetched LDPE films were examined with an EVO 18 series CARL ZESISS Scanning Electron Microscope.

FTIR analysis

The IR spectra for virgin LDPE films and chromic acid as well as Corona treated films were recorded with a Shimadzu 470 IR spectrophotometer.

Printability and ink adhesion tests

The treated LDPE film was printed with an aqueous ink (Lab 102484/14) and Solvent Based ink (Lab 102483/14) from Micro Inks Ltd. Tests of ink adhesion was performed using a standard Scotch tape adhesion test. Samples of treated film were inked using a hand anilox roller and were allowed to dry for 5 min. The test tape was applied and peeled back uniformly, and the percent ink that remained adhered to the polyethylene surface was visually estimated. The appearance of print was rated good (G) or poor (P) by considering the smoothness of ink coverage and the presence of visible pin holes. The ink adhesion was rated by hand pulling a piece of Scotch Brand 600 tape off the printed surface to determine how much ink remained on the printed surface. Zero (0.0) meant no ink adhesion, and 100.00 meant 100% of the ink adhered to the surface.

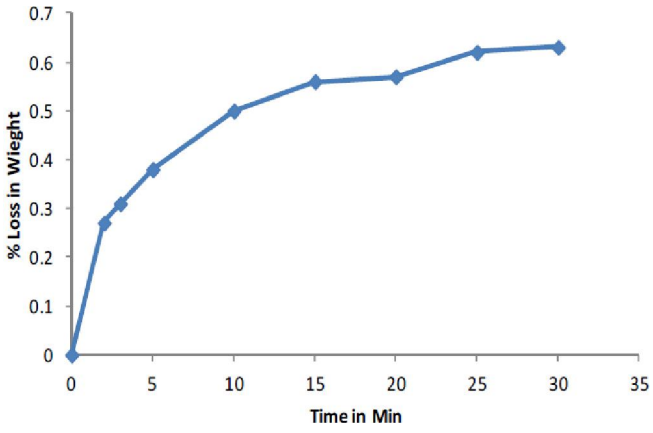

Figure 1 : % Weight loss of plasma treated LDPE film

RESULT AND DISCUSSION

Weight and thickness measurement

Figures 1 show percent weight gain at different immersion time and temperature respectively keeping the other parameter constant, we found that treatment under air results in loss of weight, which increases with time of treatment and is depicted in Figure 1. The etching process is predominant on the amorphous region of the surface than on the crystalline regions. Therefore it is possible that the initial rates of etching are more rapid. Once all the etchable amorphous materials on the surface have been removed, the remaining crystalline and tightly bound

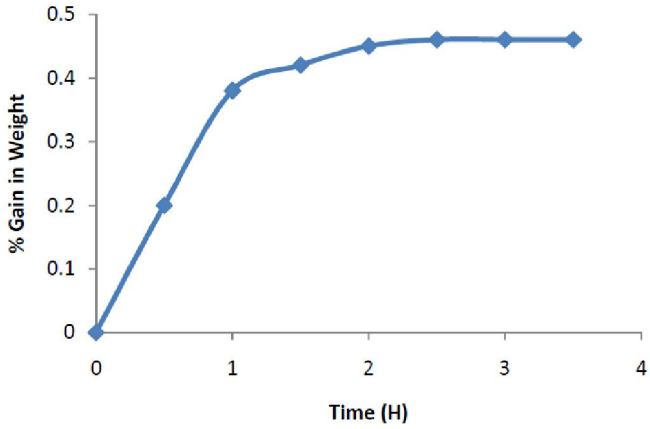

Figure 2 : The variation of percentage weight gain of LDPE film with time (at 70°C) of ammonium persulfate treated

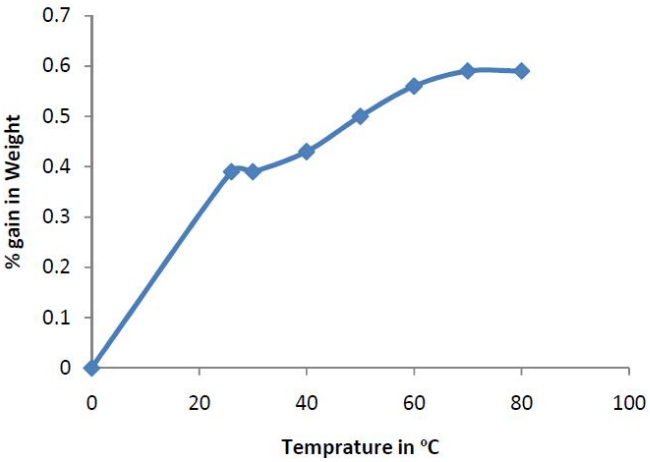

Figure 3 : The variation of percentage weight gain of LDPE film with temperature (for 3hr) of ammonium persulfate treated

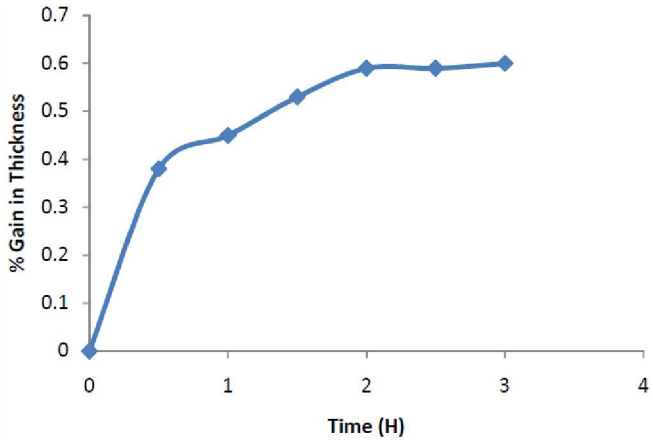

Figure 4 : The variation of percentage thickness gain of LDPE film with time (at 70°C)

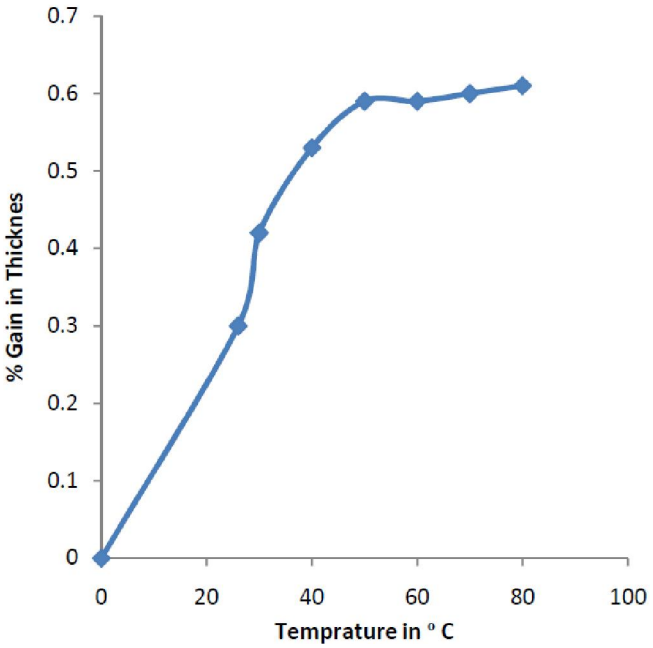

Figure 5 : The variation of percentage thickness gain of LDPE film with temperature (for 3Hr) of ammonium persulfate treated

amorphous material cannot be removed easily. Figures 2 to 5 shows percent thickness gain at different immersion time and temperature respectively keeping the other parameter constant, the weight percent and thickness for the persulfate /Fe^{+}3-treated LDPE film. From the figures it is evident that gradually the weight and the thickness of the film increase with the increase of treatment time at a constant temperature (80°C). At a constant treatment time (2.5 h), the weight of the film increases with temperature. However, both the increase in weight and the thickness of chemically modified films become asymptotic after some time

Dynamic contact angle measurement

TABLE No 1 show the dynamic contact angle measures and ink adhesion of Plasma treated LDPE films at various time. The untreated film sample had high advancing and receding contact angles which showed no adhesion with aqueous ink. The receding contact angles decreased gradually to approximately 62°.Excessive expose of a polymer film surface also lead to premature failure of the film. TABLE No 2 show the dynamic contact angle data and ink adhesion of LDPE films at various time and temperature Ammonium persulfate treatment. The untreated film sample had high advancing and receding contact angles which showed no adhesion with aqueous ink. The receding contact angles decreased gradually to approximately 66°. Excessive treatment of a polymer film surface may also lead to premature failure of the film.

SEM Analysis

Figure 6 & 7 shows SEM micrographs of Plasma untreated and treated LDPE films. Pitting and surface roughening are observed for the treated films. The improvement of wettability and adhesion of a polymer is often attributed to the increased roughness of its surface. Therefore, the pitting and surface roughness is expected to help adhesion due to increased surface area for bonding the surface modifi-

TABLE 1 : Dynamic contact angle measurements and ink adhesion of plasma treated LDPE

Plasma Treated Time (M)	Advancing Contact Angle °C	Receding Contact Angle °C	Ink Adhesion %	
			Water based ink	Solvent based ink
0	99.3	89.1	0	0
2	91.2	75.6	0	20
10	90.4	79.4	10	40
20	88.3	65.1	20	100
30	83.5	62.4	30	100

TABLE 2 : Dynamic contact angle measurement and ink adhesion of ammonium persulfate treated

Ammonium persulfate Treated		Advancing Contact Angle °	Receding Contact Angle °	Ink Adhesion %	
Time (H)	Temperature (°C)			Water Based ink	Solvent Based ink
-	70	99.3	0	0	0
0.5	70	96.7	0	0	20
2	70	92.5	10	10	50
3	70	84.6	30	30	100
3	30	95.9	0	0	0
3	40	94.2	0	0	10
3	50	89.5	86.4	0	0
3	60	82.6	76.8	10	40
3	70	85.8	66.2	20	80

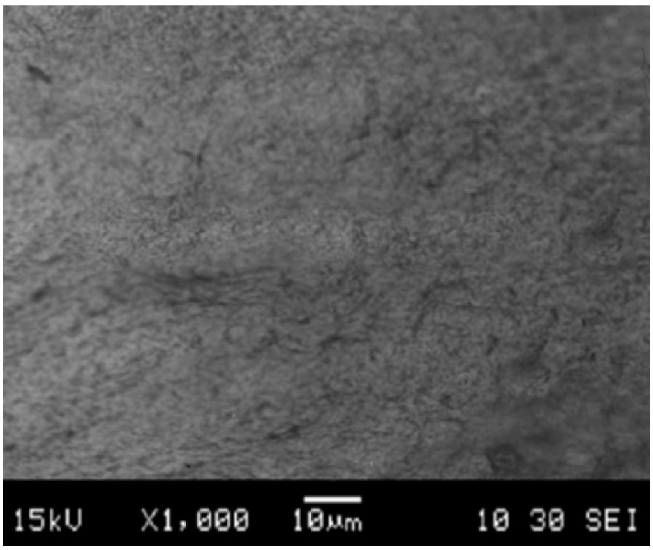

Figure 6 : Untreated LDPE film

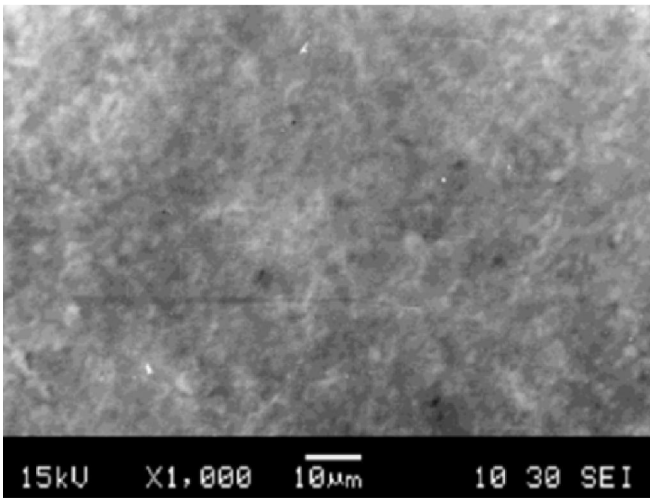

Figure 7 : Plasma treated LDPE film

cations as well as the change in topography and morphology of surface have been studied by SEM analysis. The SEM micrograph of persulphate treated and untreated LDPE films are shown in Figures 8 and 9. Pitting and surface roughing has been observed for

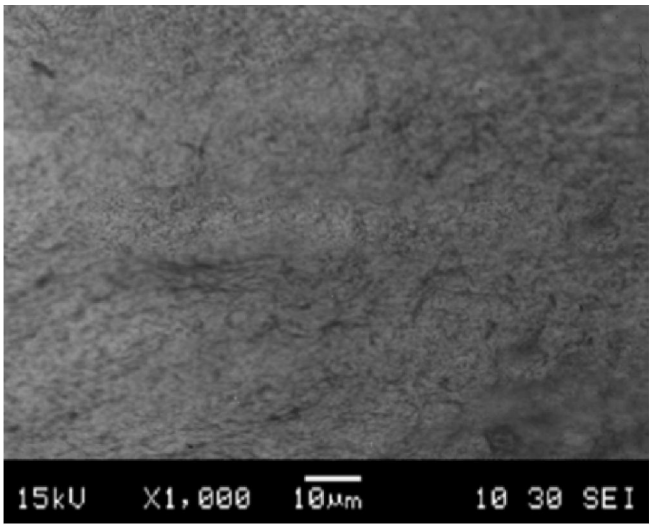

Figure 8 : Untreated LDPE film

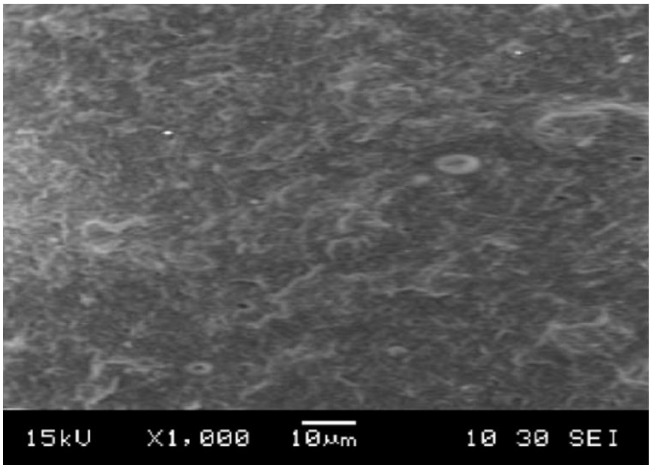

Figure 9 : Ammonium persulphate treated (70^{0}C for 3Hr)

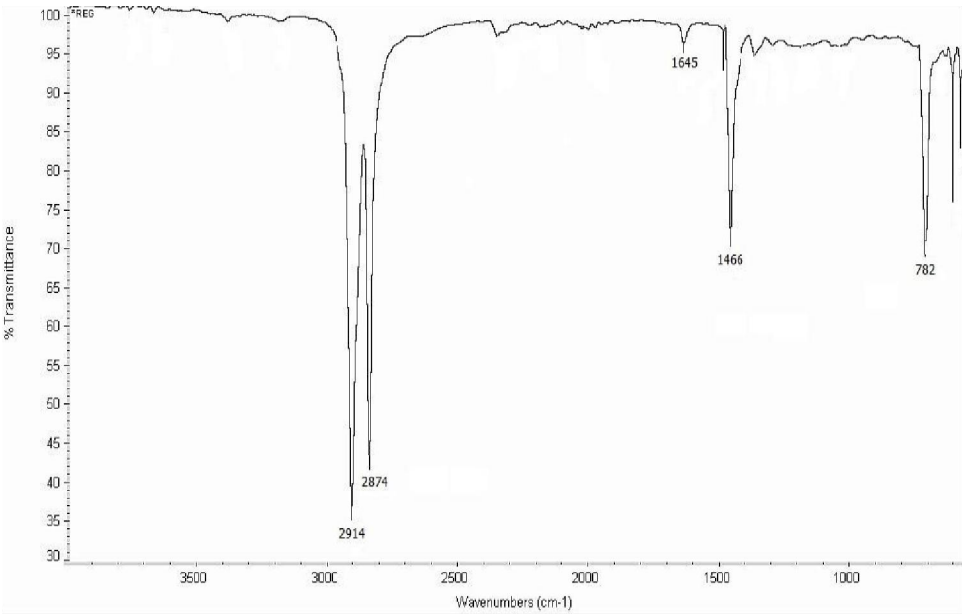

Figure 10 : FTIR of Untreated LDPE Film

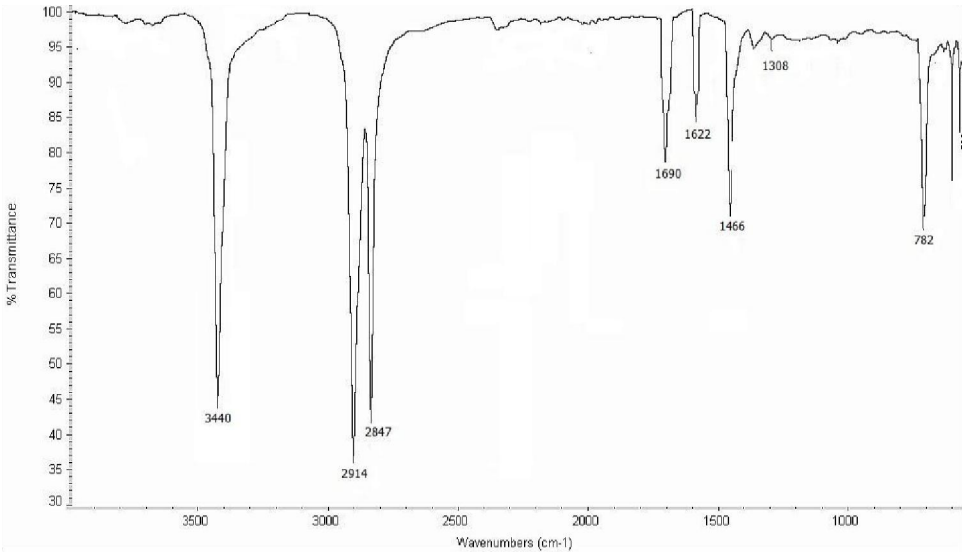

Figure 11 : FTIR of ammonium persulphate treated (70 ^{0}C for 3Hr)

the modified films. The adhesion and printability of the polymer films are improved with an increase in the roughness of its surfaces. Therefore, the pitting and surface roughnesses are expected to help adhesion due to increase in surface area for bonding.

FTIR analysis

The absorption IR spectra of modified LDPE films is shown in Figure 9 & 10 Strong bands at 1697–1700 cm^{-1}confirm the presence of >C=O of the -COOH group. At 1620–1622 cm^{-1}, this corresponds to the -CAO group adjacent to an olefinic double bond or enolic >C=O group. A strong band at 3540–3590 cm^{-1}is due to -O-H stretching. At 782–790 cm^{-1}, this corresponds to C-H bending vibration of alkenes activated due to chemical modification of the surface. At 1308–1314 cm^{-1}, this corresponds to O-H bending of the carboxylic acid group. All these absorption peaks were absent in the unmodified sample. The FTIR spectra of untreated and air plasma treated PE film are shown in Figure 9, 12, 13 shows the peak assignment PE film. When PE film is treated in air plasma the following changes take place, as shown in Figure Bands at 1697–1700 cm^{-1} confirm the presence of >C=O of COOH group and 1620–1622 cm^{-1}correspond to >C=O group ad-

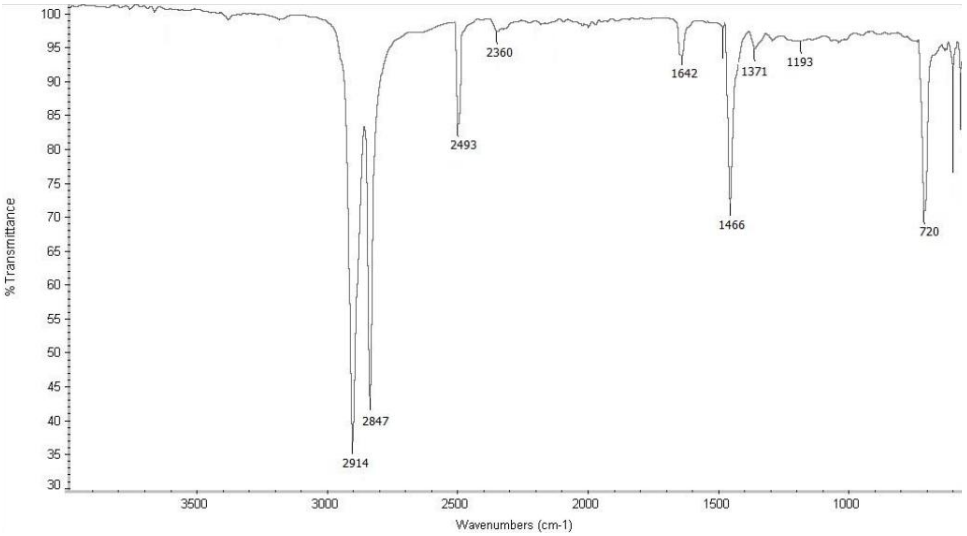

Figure 12 : FTIR of plasma treated 5 min

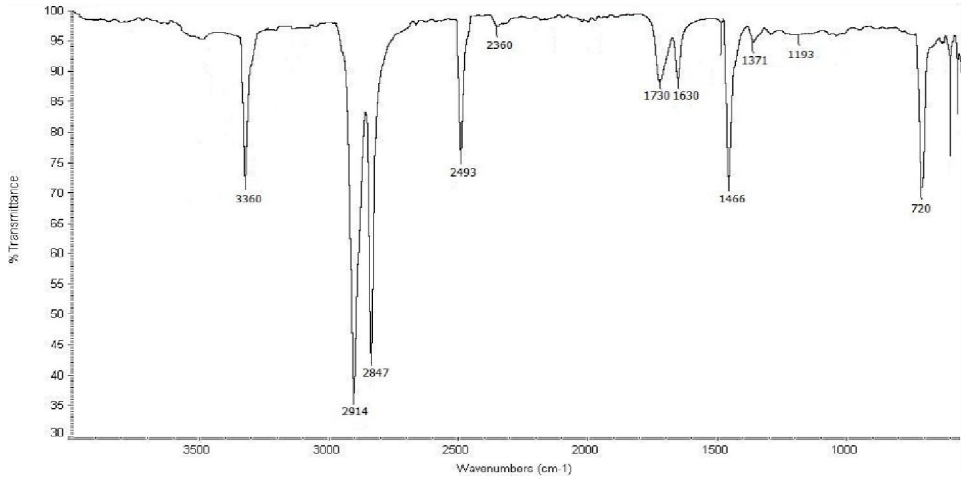

Figure 13 : FTIR of plasma treated 15 min

jacent to an olefinic double bond or enolic >C=O group. Peaks in the region 1700 and 1730 cm^{-1} correspond to C=O. Peak at 2200 cm^{-1} corresponds to>C=O group. A weak maximum at 1400 $cm^{-1}$is related to COO groups. The IR spectra of 900–950 cm^{-1} show out of plane deformation carboxyl OH as well as a small peak of alkyl peroxide at 870 cm^{-1}.24 The formation of new functional groups takes place in the remote region. OH stretching bands are observed in the region 3000–3500 cm^{-1}. Various bands are observed in the region between 1300 and 1000 cm^{-1} corresponding to C-O.

CONCLUSION

Plasma treatment and Ammonium Persulphate treatment can greatly change the surface chemistry and the topography of LDPE films. Introduction of polar groups (C=O, OH, OOH, COOH) on the surface of modified LDPE film responsible for improved ink adhesion in both corona treatment as well as chromic acid treatment. The improvement in printability is due to formation of chemical bonding between the ink and newly generated functional groups. Simultaneously, the vigorous increase of the surface roughness was found as a result of the successful treatments (as observed by SEM analysis) leads to better ink adhesion. Interlocking due to surface roughness and chemical interaction and bonding due to generation of active polar groups, as observed by ATR-FTIR studies, are accountable for excellent surface-related properties such as auto adhesion, bonding strength, ink adhesion, etc. by this type of modifications the LDPE films can be printed by

water based ink printing which is environment friendly.

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