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Comparative Study of Surface Morphology and Spectroscopic Analysis for Corona and Chromic Acid 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 Corona treatment and Chromic acid 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: Low-Density Polyethylene; Chromic Acid Etching; Corona 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 processability, 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. [7] 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. [3-4]. A number of methods have been utilized to modify the LDPE surface such as plasma treatment [19], corona treatment [15] & chemical etching [9]. In continuation of the investigation we repeat here the results of Chromic acid etching and corona 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

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. Chromic acid was freshly prepared by dissolving potassium dichromate (AR Grade, S.D. Fine Chem.) in concentrated sulfuric acid (98%) (S.D. Fine Chem.) prior to use. 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.

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centering vertical die using a Boolani blown film extrusion , blown, cooled, and collapsed to films of approximately 3-in.width.

Surface modifications

- **Corona Treatment –** A freshly made LDPE film is then immediately treated manually with a servo controlled lab Corona Treater (Model SC -450) for desired length of time. All discharge experiment was carried out at room temperature. The relative humidity was 50-60 %.

- **Chromic acid treatment –** LDPE film was cut into shape of 12 cm× 6 cm and the film samples were washed with acetone and distilled water to remove dirt and unwanted species, finally dried. The dried film samples were then etched by chromic acid at desired temperature for different periods of immersion into a bath. The temperature in the bath was maintained using temperature controller operating within ± 2^0 C. The same process was carried out, keeping immersion time constant, at different temperatures. After Chromic acid treatment the film were immediately washed with deionized water to remove excess acid and dried at 50^0 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 element 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.

Results & Discussions

Figures 1 & 2 shows percent weight gain at different immersion time and temperature respectively keeping the other parameter constant. Figures 3 & 4 shows percent thickness gain at different immersion time and temperature respectively keeping the other parameter constant. In both the cases were immersion time is kept constant the percent gain in weight and thickness is gradual over the temperature range. However, in cases where the temperature is kept constant the percent gain in thickness and weight increases at the initial stages but decreases in the later part of the test. However both the increase in the weight and thickness of etched films level off after some time.

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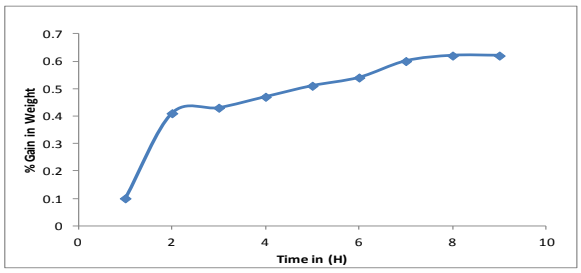

Fig. No. 1 The variation of percentage weight gain of LDPE films with time (at 26°C) of Chromic acid treated

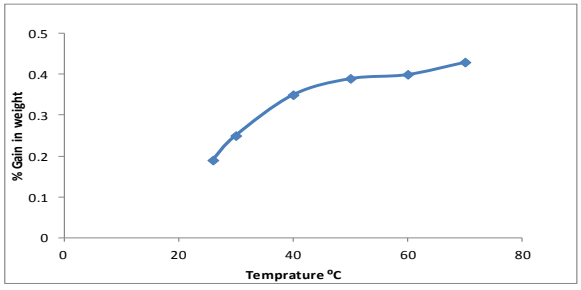

Fig.No.2 The variation of percentage weight gain of LDPE films with temperature (for 30 min) of Chromic acid treated

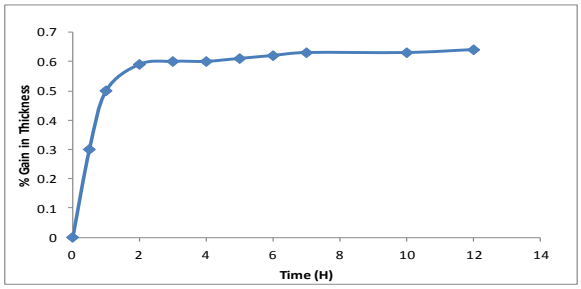

Fig.No.3 The variation of percentage thickness gain of LDPE films with time (at 26°C) of Chromic acid treated

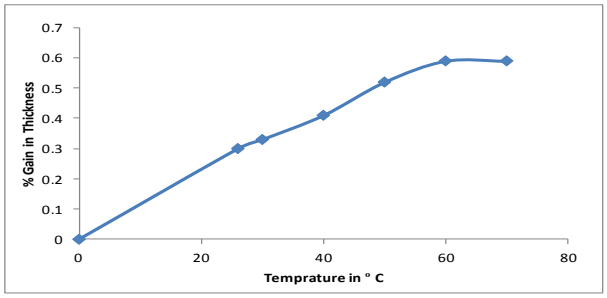

Fig.No.4 The variation of percentage thickness gain of LDPE film with temperature (for 30 min) of Chromic acid treated

$$\%\text{weight gain} = \frac{(w2 - w1)}{w1} \text{ X } 100$$

And

$$\%\text{ thickness gain} = \frac{(t2 - t1)}{t1} \text{ X } 100$$

Respectively, "1" and "2" represent the initial and final value, respectively. As the boundary between modified and unmodified is not physically distinct, the thickness is measured approximately.

In case of corona treatment the interaction of ions, electrons and energetic species of low molecular weight contaminants such as additives, processing aid and adsorb species are removed. However due to their low concentration in LDPE film the quantitative losses are negligible. Bombardment of energetic particles results in etching of the surface, due to physical removal of molecules of fragments or breaking up of bonds. [5]

Dynamic contact angle measurement

Table 1 & 2 shows the dynamic contact angles and ink adhesions of LDPE films at various corona treatment times and chromic acid treatment. The untreated film sample had high advancing and receding contact angles and showed no adhesion with aqueous ink. [21] The receding contact angles decreased gradually to approximately 64°. In case of Chromic acid it is about 65°. Proper corona treatment produces polar sites that are hydrophilic and good for ink adhesion. Excessive corona treatment is not desirable since it produces decomposition products that are insoluble in aqueous ink and do not bond to the polymer backbone.[13-14] Excessive chromic acid or corona treatment of a polymer film surface may also lead to premature failure of the film.[20]

Table no.1 Contact angle and ink adhesion of Corona treated LDPE films.

Corona Treated Time (S)	Advancing Contact Angle ^{0}C	Receding Contact Angle ^{0}C	Ink Adhesion %	
			Water based ink	Solvent based ink
0.0	99.3	89.1	0	0
25.0	90.1	76.9	0	20
50.0	89.1	78.3	10	50
100.0	86.3	67.4	25	100
200.0	83.5	62.4	30	100

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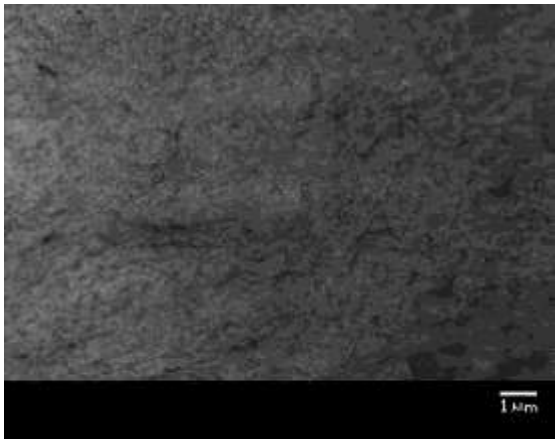
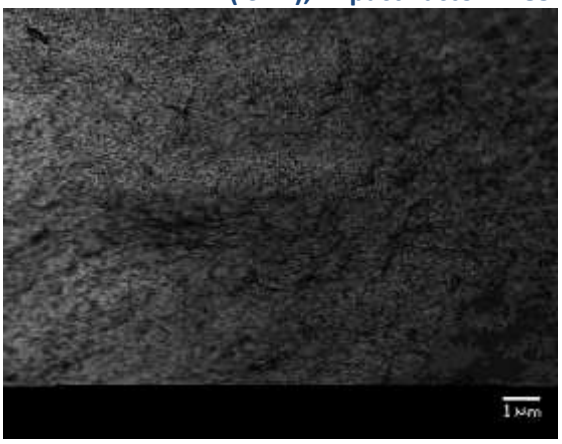
Table no.2 Contact angle and ink adhesion of Chromic acid treated LDPE films

Chromic acid Treated		Advancing Contact Angle ^{0}	Receding Contact Angle ^{0}	Ink Adhesion %	
Time(H)	Temp (^{0}C)			Water Based ink	Solvent Based ink
-	26	99.3	89.1	0	0
0.5	26	95.8	88.5	0	0
2	26	93.2	79.4	10	30
4	26	92.8	65.8	35	50
6	26	87.6	69.2	30	100
10	26	86.4	65.3	45	100
0.5	30	95.9	94.5	0	0
0.5	40	94.8	92.3	0	20
0.5	50	94.5	86.4	5	70
0.5	60	82.6	76.8	20	100
0.5	70	85.8	66.2	40	100

SEM analysis

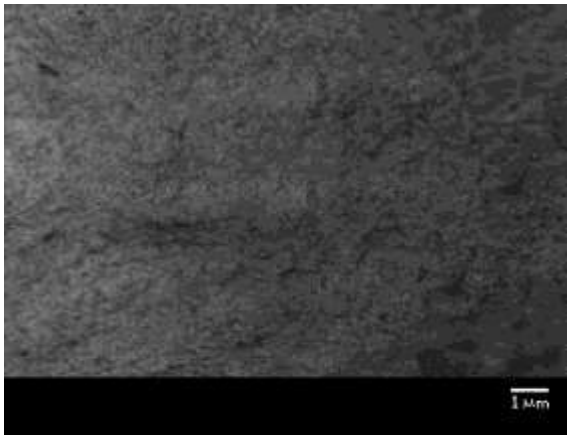
SEM-EVO18 series by Carl Zesiss is used to study the surface morphology by means of micrographs of chromic acid treated untreated and corona treated-untreated LDPE films are shown in Figure Pitting and surface roughening are observed for the treated films. The improvement of wettability and adhesion of a polymer is often attributed to the increased roughness of its surface.[6-11] Therefore, the pitting and surface roughness are expected to help adhesion due to increase surface area for bonding.[2]

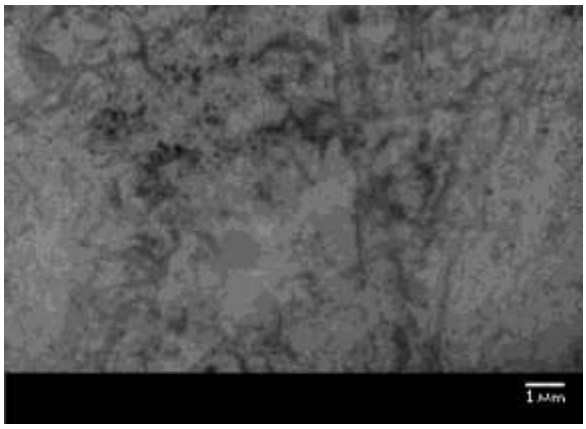




(a) (b)

Fig. No. 5 –SEM images of untreated (a) and corona treated (b) LDPE films





(a)(b)

Fig. No.6- SEM Images of untreated (a) Treated 60^{0}C for 30 min (b) LDPE sample

FTIR analysis

It is well known that corona treatment incorporates hydrophilic functionality on polymer. To confirm the changes in the chemical structure,

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analysis of LDPE films via FTIR spectroscopy was done. The FTIR spectra of untreated and corona treated PE film are shown in Figure 7.When PE film is corona treated there are presence of bands at 1670–1700 cm^{-1} confirm the presence of C=O of -COOH group and A band at 1630 cm^{-1} is assigned to ethylenic double bonds C=C and the other at 1720 cm^{-1} is characteristic of carbonyl groups. OH stretching bands are observed in the region 3000–3500 cm^{-1}). IR spectroscopy has been used to study the changes occurring upon chemical modification and/or oxidation of LDPE film by chromic acid. The IR spectra of chromic acid-treated and untreated LDPE films are shown in Figure no 8. The appearance of strong bands at 1700–1712 cm^{-1} confirms the presence of C=O of -COOH group. A strong band at 3580–3590 cm^{-1} is due to the OOH stretching. The appearance of a strong band at 1170–1180 cm^{-1} is assigned to the S=O group of sulfonic acid.

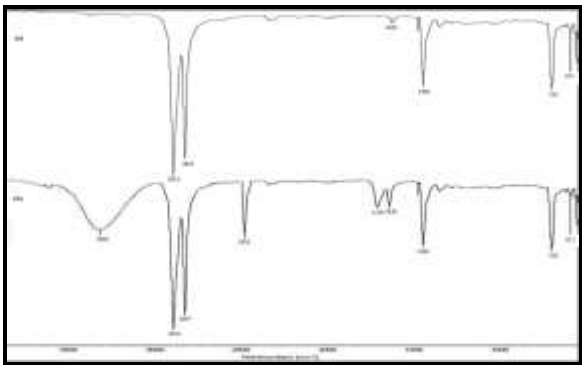

Fig. No. 7 –Untreated (a) corona treated (b) LDPE film (20 Sec)

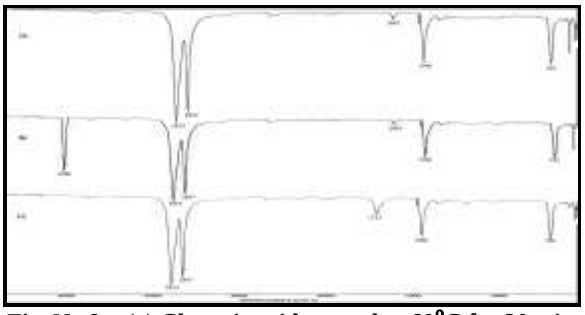

Fig. No.8 - (a) Chromic acid treated at 60^{0}C for 30 min (b) Chromic acid treated at 26^{0}C for 12 Hr (c)

Printability Test

LDPE films permanent printing is difficult because of its non polar nature where as printing inks are usually polar, introduction of polar groups onto the surface of LDPE film helps to enhance printability [16-17].Unmodified LDPE film sample have no printability. Appreciable improvement is observed by treatment with corona and chromic acid in the printability. The introduction of polar groups by oxidation in corona and etching with chromic acid enhanced printability. [10-12]

Conclusion

Corona treatment and chromic acid 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 autoadhesion, 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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