Biodegradable Film. IV. Printability Study on Biodegradable Film

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ABSTRACT: A starch-based biodegradable (BD) low density polyethylene (LDPE) film can be directly printable without any corona treatment, unlike virgin LDPE film. Such a film shows poor adhesion and nail scratch resistance of the ink on the printed area of the film. In order to increase the adhesion and nail scratch resistance of the ink on the printed BD film, grafting of acrylonitrile onto the BD film is carried out. The polyacrylonitrile grafted BD film shows better adhesion, nail scratch resistance, and printability. The printability of the polyacrylonitrile grafted BD film is comparable to the conventional corona treated LDPE film. The extent of printability is a function of the surface smoothness, as well as the optimum percentage of grafting on the biodegradable film. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1273–1277, 2001

Key words: biodegradable film; printability; acrylonitrile; starch; low density polyethylene; graft copolymerization

INTRODUCTION

Polyethylene (PE) is one of the most widely used commodity polymers in the market. Because the PE surface shows poor adhesion to ink and other polar agents, printing on the PE film requires some physical and or chemical treatment such as corona discharge,[1] plasma discharge,[2] chemical etching,[3] chemical modification,[4] and so forth. Some reactive functional groups that have affinity for dyes and pigments are generated that are due to such chemical treatment. It was reported that the dyeability of chemically modified cellulose is much better when compared with unmodified cellulose.[5–7] The chemical modification of cellulose was done by cyanoethylated cellulose, carboxy methylated cellulose, cellulose grafted with polyacrylonitrile (PAN), and poly(methyl methacrylate).[8]

In a starch-based low density PE (LDPE) biodegradable (BD) film, starch is polar and hydrophilic. The presence of polar starch molecules in the BD film increases its dye affinity and therefore the BD film can be printed without any modification. However, the nailscratch resistance of such printed films is poor.

In order to generate more polar groups on the starch-based BD film, the graft copolymerization technique can be used. The presence of starch in the BD film can be used for graft copolymerization by generating free radicals on the starch backbone and then allowing these macroradicals to react with vinyl monomers.

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Acrylonitrile (AN) was recently graft copolymerized onto the surface of a starch-based BD film.[9] The AN grafted BD film (AN-*g*-BD) is more polar than a virgin BD film, and it is expected that such grafted films will show better printability and nail scratch resistance. The detailed investigation of the printing of a BD film, as well as an AN-*g*-BD film, is described in this communication.

EXPERIMENTAL

Materials

A starch-based PAN grafted BD (PAN-*g*-BD) film, Brite flex standard red ink (polyamide based), and polytone standard red ink (nitrocellulose based) supplied by Coates India Ltd., Calcutta, were used for printing.

The detailed procedure for the preparation of a starch-based BD film is discussed elsewhere.[9,10]

Printability Test

The printability test was carried out with an Auto Gravure Proofer RK Print Coat instrument, using a Gravure etched plate of screens with 120 lines/in. A film coated with polyamide-based Brite flex ink was air dried with hot air (~60°C). The adhesion and the nail scratch tests were carried out immediately after drying and at 24- and 48-h intervals. The ink adhesion to the film was evaluated qualitatively using tape coated with a pressure-sensitive adhesive. Adhesion was considered good in cases where the tape adhesive stuck to the ink film and there was no failure in the ink film interface. The above-mentioned printed film was compared with the naked eye with a standard corona treated LDPE film printed with the same ink to determine the comparative rating of the printability aspects of the film.

Methods for Modification of BD Film

In order to impart the effect of printability on the BD film, the following modification treatments were applied on the virgin PAN-*g*-BD films.

High Energy γ-Ray Radiation

The PAN-*g*-BD films were exposed under Co^{60} γ radiation in a gamma chamber (model 900, BARC, Bombay) with a radiation dose rate of 15.4128 krad/h for 360 h.

UV Radiation

The PAN-*g*-BD films were exposed to UV radiation under a 400-W high-pressure mercury lamp (Phillips, India) that was placed at a distance of 46 cm away from the film surface for 12 h.

Thermal Treatment

The PAN-*g*-BD films were exposed in an aging oven at 70°C for 48 h.

Table I Printability and Adhesion Test of LDPE, Corona Treated LDPE, Ungrafted BD, and Grafted BD Film

		Immediate Tape Adhesion		After 24-h Tape Adhesion		After 72-h Tape Adhesion	
Film Type	Printability	Slow Pull	Hard Pull	Slow Pull	Hard Pull	Slow Pull	Hard Pull
Untreated LDPE	8	0	0	0	0	0	0
Corona treated LDPE	10	10	10	10	10	10	10
Ungrafted BD film	9	0	0	0	0	0	0
18% PAN-*g*-BD film	3	10	7	10	9	9	9
8% PAN-*g*-BD film	8	8	7	8	8	10	9

The results qualified visually with gradation 10 for the best and 0 for the poorest.

Table II Variation of Printability, Adhesion, and Nail Scratch Resistance of PAN-*g*-BD Film with Percentage of PAN Grafting

PAN Grafted Film (%)	Surface Smoothness	Printability	Immediate Tape Adhesion		Nail Scratch Resistance
			Slow Pull	Hard Pull	
0 (Basefilm)	10	10	0	0	0
3	8	9	7	6	6
6	7	9	8	8	8
8	6	8	1	2	3
10	4	6	7	7	7
12	1	3	9	9	7
14	1	3	7	7	8

The surface smoothness qualified visually with gradation 10 for the best film and 0 for the poorest film.

Hydrolytic Treatment

The PAN-*g*-BD films were hydrolytically treated at 80°C for 6 h.

RESULTS AND DISCUSSION

The printability and adhesion test results for the PAN-*g*-BD film, untreated BD film, and corona treated LDPE film are presented in Table I.

The ink adhesion to the ungrafted BD film (base film) was poor, although the printability of the film was good. This indicated the lack of sufficient functionality on the BD film surface for good ink adhesion. Although in a BD film the starch polar component is present, the starch granules are intimately blended in the matrix of the PE. Moreover, in the film extrusion process at a temperature of around 150°C most of the starch granules are coated with a thin coating of PE, leaving only a few granules uncoated. These uncoated starch granules with their polar groups are insufficient for good adhesion to ink. The printability of the ungrafted BD film is good (i.e., the ink wet the polymer surface better). Wetting also depends on the surface smoothness. Wetting is necessary for printing, but it is not a sufficient condition for ink adhesion.[11]

The variation of the printability, immediate tape adhesion, and nail scratch resistance of the ungrafted BD film (base film) and the PAN-*g*-BD film with the percent of grafting are presented in Table II.

Table III Printability, Adhesion, and Nail Scratch Resistance of Untreated BD Film and 18% PAN-*g*-BD Film after Different Treatments

Physical Treatment	Film	Printability	Adhesion		Nail Scratch Resistance
			Slow Pull	Hard Pull	
γ-Ray irradiation, 360 h, RT	BD	10	10	9	0
	PAN-*g*-BD	7	10	10	9
UV-Ray irradiated, 12 h, RT	BD	10	5	4	0
	PAN-*g*-BD	9	10	9	9
Hydrolytic treatment[a]	BD	8	0	0	0
	PAN-*g*-BD	9	9	9	9
Thermal treatment[b]	BD	8	0	0	0
	PAN-*g*-BD	7	10	9	9

[a] Water treatment at 80°C for 6 h.
[b] Thermal treatment at 70°C for 48 h.

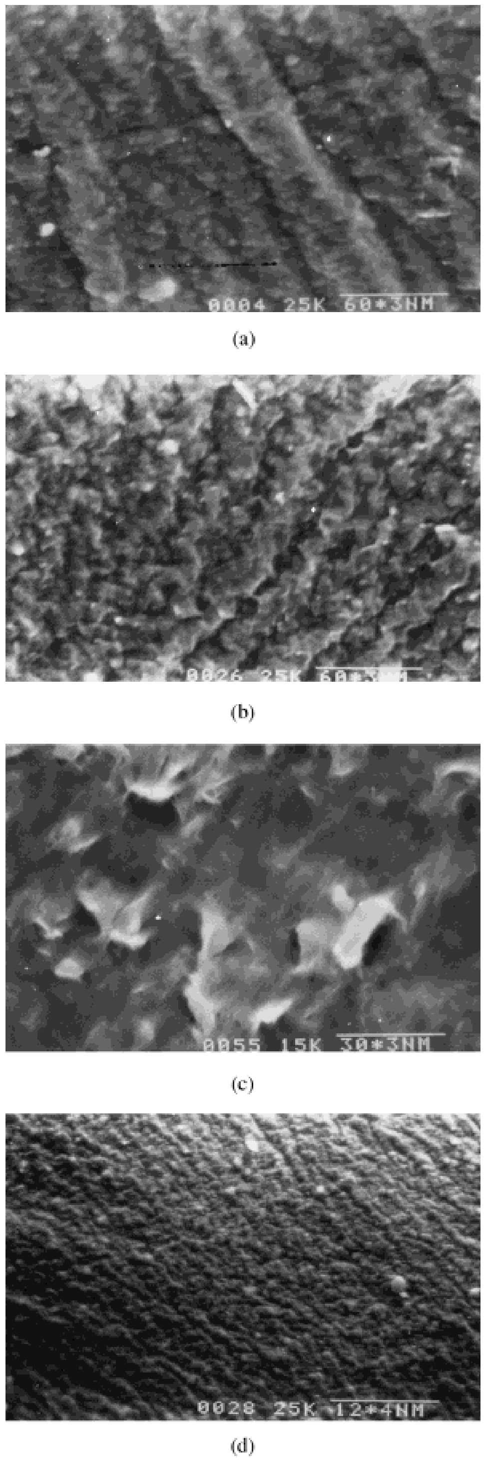

Figure 1 SEM micrographs of (A) UV-ray irradiated BD film, (B) γ-ray irradiated BD film, (C) 18% PAN-*g*-BD film, and (D) virgin BD film.

The grafting of AN onto the BD film reduces the surface smoothness and increases the thickness. Because the printability depends on the surface wetting of the ink, the increase in the surface roughness of the ink does not effectively cover the film surface.[12–15] As a result, the printability decreases with an increase in the percentage of grafting. As the percentage of grafting increases the polar cyanide group on the surface also increases, so the adhesion of the ink to the film surface increases. The nail scratch resistance is related to ink adhesion, which also increases with the percentage of grafting of AN onto the BD film.

The printability, adhesion, and nail scratch resistance of the untreated BD film and the PAN-*g*-BD film after UV irradiation, γ-ray irradiation, hydrolytic treatment, and thermal treatment are presented in Table III.

The ink adhesion to the γ-ray treated BD film and the UV-ray treated BD film was better than that of the untreated BD film and comparable to the PAN-*g*-BD film. However, the printability of the γ-ray and the UV-ray irradiated BD films was better than the PAN-*g*-BD film, because the wetting of the ink to the ungrafted BD film was much better than the grafted BD film.

The SEM micrographs of the γ-ray irradiated BD film, UV-irradiated BD film, 18% PAN-*g*-BD film, and BD film are presented in Figure 1. Pitting and surface roughening are observed for the treated films. The improvement of the ink adhesion is attributed to the increased roughness of the film surface.[16] Therefore, the surface roughness is expected to help adhesion because of the increased surface area for bonding and mechanical interlocking.

IR spectroscopy was used to study the changes occurring with the γ-ray treatment and/or oxidation of the BD film. The IR spectra of the γ-ray treated and untreated BD films are shown in Figure 2. From the IR analysis of the γ-ray treated BD films [Fig. 2(A)] the appearance of a bond at 1700 cm^{-1} confirms the presence of a >C═O of the COOH group. A band at 1664 cm^{-1} corresponds to a >C═O group adjacent to an olefinic double bond or an enolic >C═O group. The strong band at 3374–3483 cm^{-1} is due to —OH stretching.

Because the γ-ray treatment of the BD film introduces several oxygen adducts to the film surface, the anchorage of the polyamide-based ink is better. Here actually the H-bond formation between the enolic hydroxyl groups of the film surface and the carbonyl group of the ink increases adhesion.

The use of nitrocellulose-based polytone ink and polyamide-based Brite flex ink for printing on the film showed more or less the same result, but

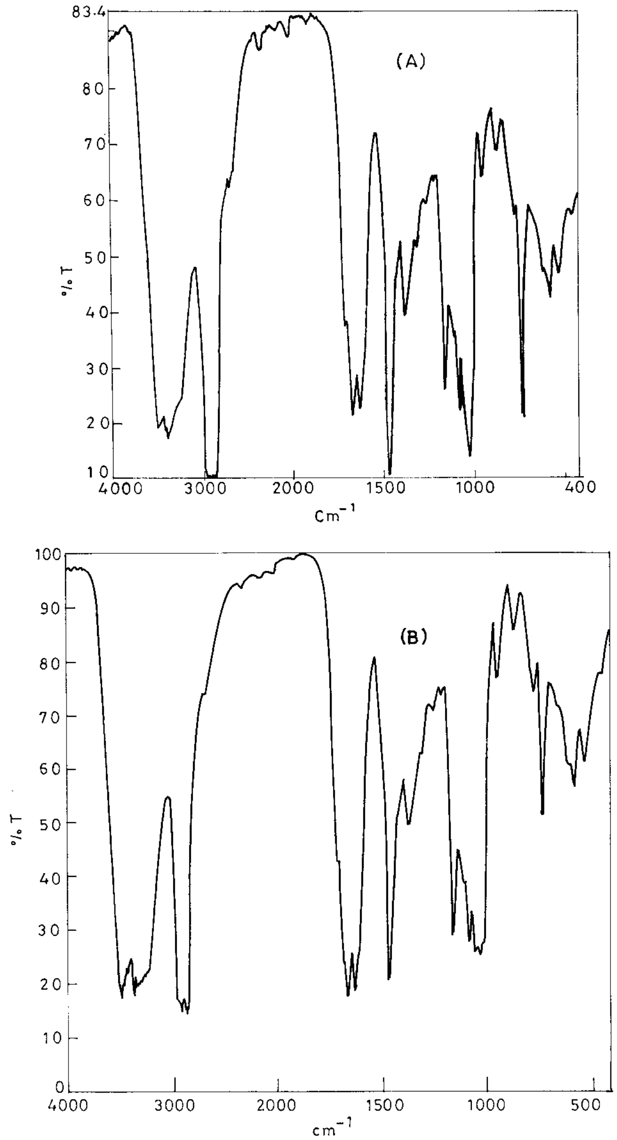

Figure 2 IR spectral of (A) a γ-ray irradiated BD film and (B) an untreated BD film.

the nitrocellulose-based ink imparts less gloss than the polyamide-based ink.

CONCLUSION

Because of the presence of starch in the BD film, the BD film, unlike virgin LDPE on other plastic films, is printable without any expensive corona treatment. The ease of printability of the BD film can be further enhanced by adding suitable additives. Grafting of such starch blended LDPE film (BD film) with AN resulted in the ability to print onto the film by way of developing functionality on the film surface. Ink adhesion, nail scratch resistance, and so forth, are the properties of printing that can be improved by this modification and open up the possibility of its use in packaging.

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