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Resistance Properties of Printed Polyolefin Films using Water-Based Inks

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ABSTRACT

In this research, two acrylic emulsion resins and an adhesion promoter polyester emulsion resin were used to optimize water-based printing ink formulation for printing on polyolefins. Then, resistance properties of printed films were evaluated. The used polyolefins were transparent polypropylene, transparent and opaque polyethylene. Adhesion of samples increased from polypropylene to polyethylene while opaque polyethylene had better adhesion compared with transparent one. However, scratch resistance and optical properties of samples were independent of the substrate. SEM images showed that the samples with Zinpol 350 had larger structure which caused the gloss decrease while for samples containing Glascol LS26 high level morphology and small microstructure lead to higher gloss and adhesion properties. Prog. Color Colorants Coat. 8 (2015), 207-217 © Institute for Color Science and Technology.

1. Introduction

During recent decades, due to the increase in pollutants release from various industries, reduction or elimination of volatile organic compounds (VOCs) has become one of the main purposes of researches in order to protect the environment. VOCs are substances which contain carbon and evaporate readily; nevertheless some materials such as carbon oxides are not generally classified as VOCs [1]. Most of solvents used in paints and coatings, inks, adhesives, cosmetics and laminations are considered as VOC's, so these industries have been going to use high solid, water-based, powder and UV-curing systems. Water-Based ink has become a new research hotspot due to its printability and environmental friendliness [2]. Water-based systems are good alternatives for solvent-based systems and acrylic resins are the most widely used polymers in water-based systems in paints, coatings and printing inks. Polyethylene and polypropylene are

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frequently used as printing substrates. Polyolefins are generally known to be very difficult painting substrates [3] because of their low surface energy and consequently, poor wettability. The presence of a weak boundary layer has also been suggested as a possible reason for the lack of good adhesion between polyolefins and coatings [4]. A polyolefin film is a non-absorbing substrate, which makes it difficult to optimize the drying process. This is another important factor in the use of polyolefin as a printing substrate [5]. Acrylic resins have several advantages over other polymers such as improved flexibility and adhesion properties, transparency, resistance to yellowing, high gloss and gloss retention, resistance to chemicals and outdoor durability [6]. Presently, there are three physical forms of acrylics: solid beads, solution polymers and emulsions. The emulsion is the dominant form which is used today [7].

Emulsions can be characterized according to some physical features such as solid content, viscosity, pH, particle size and minimum film forming temperature. Emulsion particle size differs from 0.05 to 0.5 μm, depending on type and amount of surfactant used. However, surfactants cause higher water sensitivity of the dried film but stability of the emulsions is resulted by them [6, 7].

Film formation is a key factor in water-based emulsions for achieving good properties. Film forming process can be divided to three main stages: flocculation, coalescence and autohesion. Despite all particles still have their own identity and the polymer film is still reversible in flocculation stage, the polymer particles start to coalesce in stage 2. In this stage, the polymer film is not soluble in the water anymore so it is not reversible [8]. Coalescence stage can be affected by emulsion particle size, film forming temperature, co-solvents, functional group in polymer, glass transition temperature (T_g) and Minimum Film Forming Temperature (MFFT) [6].

One of the most important properties of ink for good press performance is resolubility, i.e. the ability of ink to re-dissolve the dried ink film by itself. In solvent-based polymers, because of dried film's ability to remain soluble in their solvent, resolubility is very high. However, in water-based systems, resolubility is relatively low because of negative effect of especial film formation process [8].

Once choosing material for water-based ink formulation, a proper blend of polymers must be selected to achieve a good balance between reversibility and printing resistance properties. Reversibility is essential for high press speed printing specially in flexography and gravure in which ink should not become dry on cylinder to obtain clean and sharp images in long print runs. To achieve reversibility, a solution resin with high acid value is used in ink formulation. However high acid value reduces resistance properties of ink film, it makes inks more reversible and increases pigment wetting [8, 10].

Conventional acrylic emulsion polymers have had an oligomeric structure with molecular weight less than 50,000 and a hydrophobic backbone. They showed properties such as good resolubility, low MFFT, excellent compatibility with other acrylic resins and pigment wetting properties but because of their hydrophobic structure, their resistance properties were not so desirable and their drying speed was slow due to their low solid content (20-30%) [8].

New types of polymers were developed for water-based printing inks to remove these defects. These groups of resins, named self-crosslinkable polymers, are made from a blend of oligomers with polymers. In these systems, oligomers stabilize emulsions in polymerization processes as surfactant. Because of higher molecular weight of polymers than oligomers and their hydrophilic nature, they show better resistance properties and block resistance [8].

For self-crosslinkable resins, resolubility is maintained constant due to oligomer presence in combination with polymer particles and solid content will be promoted (40-45%) because of better mass/volume ratio and decreased vacant space. This high solid content causes better drying profile but it is not enough yet. So a co-solvent may be needed for better film formation which in turn is not pleasant for environment [8, 10, 12].

Actually, self-crosslinkable resins containing styrene-acrylic compounds were introduced to promote resistance and adhesion of ink binders to flexible packaging films and foils. Chemical structure and promotion of polymeric network improves the adhesion as well as water and block resistance. All in all, this type of inks exhibited improved performance in comparison to conventional inks [8, 10, 12].

Besides resins, solvents have an important role in ink formulation for achieving good printing properties. Solvent adjusts the ink viscosity and allows ink to be transferred from plate to substrate. Water is the main solvent in water-based inks, but for better film formation, a percentage of organic solvent like alcohols, glycols or glycol ethers can be added to ink formulation [6, 11].

The scope of the present work is to evaluate the effect of surfactants (Zinpol 350 and Glascol LS26) and different types of resins in the resistance properties of printed polyolefin films using water-based inks.

2. Experimental

2.1. Material

A solid styrene/acrylic resin from BASF with high acid value was used in this project for pigment dispersion. Two letdown emulsion resins from BASF and Worlee were utilized for producing water-based ink. An aqueous polyester emulsion resin from Evonik was also used as an adhesion promoter in formulations to study the effect of its concentration on polyolefin/ink adhesion. The specification of these resins is presented in Table 1. Water-based inks ingredients are listed in Table 2. Variable parameters in this project were letdown resin, adhesion promoter resin percentage and polyolefin substrate. Pigment Blue 15:3 (supplied by M.O.L, India) was used as colorant in this study.

2.2. Preparation of substrates

All Polyolefin substrates (supplied by Nylon Sepid Mfg. Co, Iran) used in this project were untreated and their specification is shown in Table 3. Substrates were treated with corona in an optimum condition which is found at power of 480 Watt and speed of 20 m/min by corona treatment instrument.

Table 1: Resins Specification.

Resin	Supplier	Role	T_g (°C)	Solid Content (%)
Joncryl HPD 678	BASF	Grinding	101	99
Zinpol 350	Worlee	Letdown	0	45
Glascol LS26	BASF	Letdown	22	46
EPDS 1300	Evonik	Adhesion Promoter	---	45

Table 2: Water-Based Ink Components.

Component	Content	Comment
Pigment	35%	---
Emulsion polymer	---	Letdown resin
Water	---	solvent
PE Wax	---	---
Antifoam	---	---
Amine	14.45 g	pH adjustment
Polyester resin Delta-S 5225	---	Adhesion promoter Wetting agent

2.3. Preparation of samples

The solid resin with high acid value was dissolved in water together with ammonia as grinding resin. The pigment paste with fine particle size was achieved by mixing the pigment, solution resin, water and wetting agent in a pearl mill for two hours. Then, the letdown resin was mixed with the pigment paste. Finally, additives were added to the ink. Flow time and pH of the ink were adjusted by adding water and amine, respectively. Flow time was adjusted to 18±1 second by Ford cup #4 using ISO 2431:2011. Triethanolamine was used as an amine to adjust the pH of each ink to 8±0.5.

2.4. Inks printing and evaluations

RK Print coater lab instrument (model K202) was used to print samples on polyolefin films. Thickness of K-bar and speed of printing was four microns and 10 m/min, respectively. Tests were done after the printed films were dried at room temperature for 24 hours. But main control of inks was done on dried printed films. The durability and appearance of printed ink films were evaluated individually. Surface tensions of liquid printing inks were measured by Tensiometer K9 (KRÜSS, Germany). The adhesion quality test was assessed simply by a tape test using tesa-tape, which was attached firmly to the print and peeled off rapidly by hand [13]. One test on two different overprinted strips was carried out for each sample 48 h after printing. Adhesion was quantified by image analyses of the mark on the overprinted ink film and this was compared with the mark on the ink film of the original ink [14].

For determination of scratch resistance of each sample, fingernail was used with a typical pressure and fast movement. Then by analyzing the tested area, percentage of remaining area was reported as scratch resistance. For each sample, the measurements were repeated five times and their average value was reported. The print density of inks was measured by a Techkon SD620 densitometer (Techkon GmbH, Germany) with 3.2 mm measuring port diameter. Here again, the measurements were repeated five times for each sample at various spots of the printed film and the average value was reported. Gloss of printed inks according to ASTM D523 was measured by Sheen Tri-glossmeter. The average of five measurements at degree of 60 was reported. Friction coefficient of printed ink was obtained by friction lab instrument (Erichson, Germany) with speed of 0.5 m/min. The thickness of printed inks was 4 μm and the test was done after 24 hours. The measurement was done three times for each sample and the average was reported.

The morphology of printed ink film was determined by electronic scanning microscopy (Seron Technology SEM device model AIS D-5264). In order to determine the resolubility of the inks, a drop of ink was poured on a printed film and it was wiped with a wet napkin after a few seconds. If the resolubility of ink is appropriate, the printed parts under the drops of ink will be cleared. The minimum time needed for wiping the whole printed film away was measured by chronometer and reported in seconds.

Table 3: Polyolefin Films Characteristics.

Substrate	Appearance	Thickness (μm)	Material
Polypropylene	Transparent	50	PP
Polyethylene	Transparent	100	LDPE
Polyethylene	Opaque	50	LDPE

3. Results and discussion

3.1. Ink surface tension

Table 4 shows the surface tensions of samples. The results show that the surface tension of inks changed with exchanging letdown resin in formulation. The inks with Glascol LS26 have higher surface tension than inks containing Zinpol 350. Furthermore, in all case, the surface tensions of inks increase with adding adhesion promoter resin in formulation. Actually, for every letdown resin, the surface tension of inks increase to a same value equal to about 39.6×10^{-3} N/m with increasing the percent of adhesion resin to six.

3.2. Print evaluation

Figure 1 shows the effect of letdown resin and adhesion promoter on adhesion and scratch resistance of printed inks. The maximum standard deviations of scratch resistance and adhesion for each sample were 13.2 and 12.5, respectively. As shown in Figure 2, the print adhesion of all samples on transparent polyethylene (PE) was excellent. However on opaque polyethylene and polypropylene (PP), only the adhesion of inks containing Glascol LS26 was good and inks containing Zinpol 350 had the worst adhesion. Moreover, adding the adhesion promoter resin did not influence the ink-substrate adhesion too much. As a result, inks adhesion increased from PP to opaque PE and then transparent PE (best). In addition, samples containing Glascol LS26 in their formulation showed the best adhesion of inks on polyolefins. Functional groups in resin structure had an important role in printing ink adhesion to polyolefin films. The existence of styrene groups in letdown acrylic resin structure improved adhesion and resistance properties of dried ink films. Carboxylate groups have more physical and chemical bond to polyolefin substrates and so show higher adhesion in contrast to styrene groups. Nevertheless, due to lack of functional groups on polypropylene substrate, there were a little of chemical bonding between ink and PP that made the adhesion to decrease. However, adding of polyester resin to ink formulations did not help to increase the adhesion between substrate and ink.

On the other hand, these inks despite of their best adhesion properties did not have enough scratch resistance on PP. Moreover the addition of adhesion promoter resin decreased their scratch resistance. Nevertheless, the scratch resistances of all samples containing Zinpol 350 were extremely good except on opaque PE which was medium. Even for PE substrate, the scratch resistance of inks containing Glascol LS26 is acceptable. So we can conclude that the addition of adhesion promoter resin to the ink formulation did not affect the ink-substrate adhesion and adversely decreased the scratch resistance of inks that their letdown resins were Glascol LS26.

Table 4: Surface tension of inks (N/m×10^3).

EPDS (%) Letdown resin	0	3	6
Zinpol 350	38.43	38.90	39.57
Glascol LS26	39.37	39.70	39.60

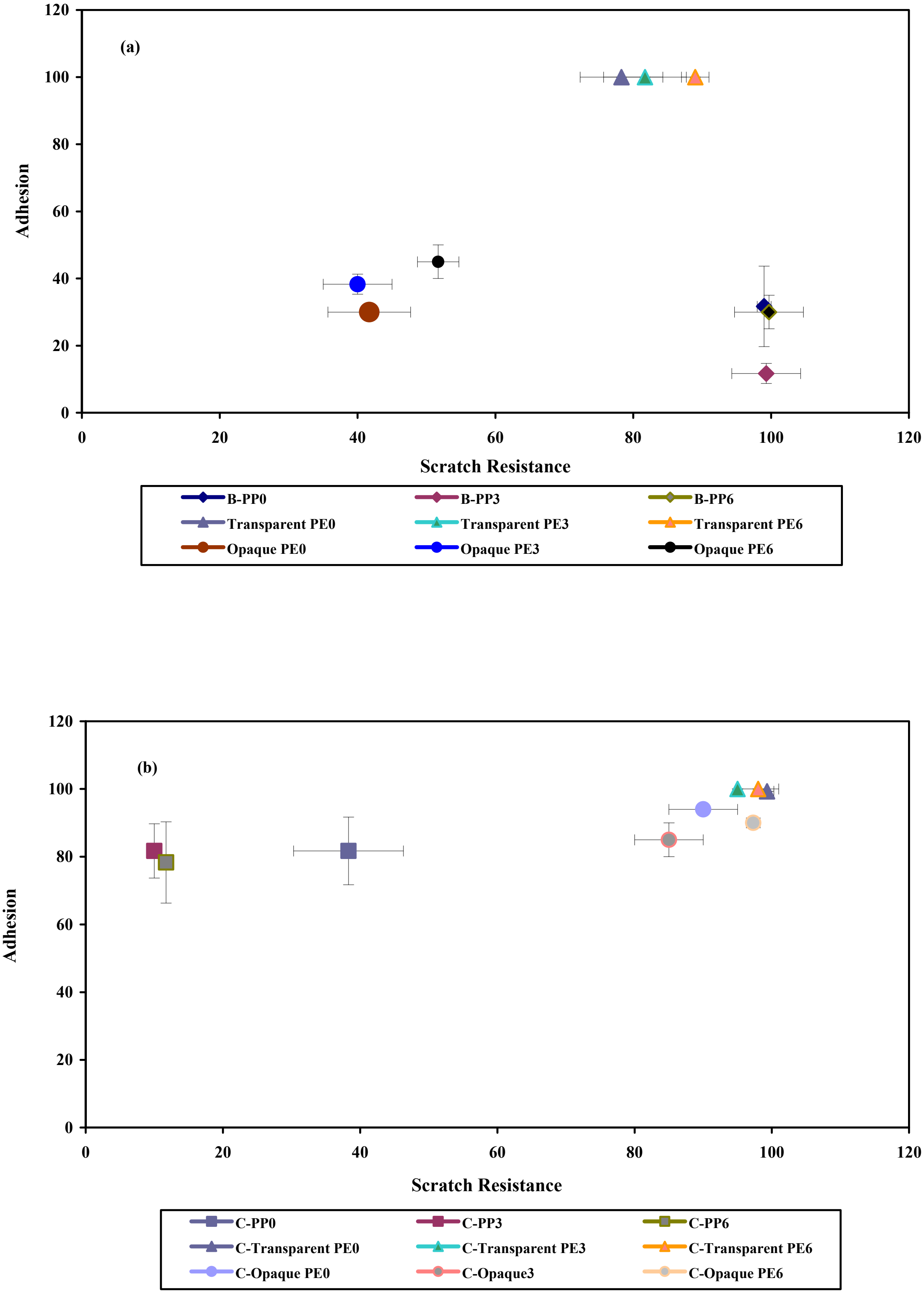

Figure 1: Adhesion versus scratch resistance plots for three substrates, (a) Zinpol 350, (b) Glascol LS26.

In Figure 2, the gloss and print density of all samples are illustrated. This Figure can show the effect of letdown resin and adhesion promoter percentage in ink formulation on optical properties of the printed films. It should be mentioned that the standard deviations of gloss and print density reached a maximum quantity of 4.5 and 0.1, respectively. According to Figure 4, it can be concluded that inks containing Glascol LS26 had higher gloss in comparison to Zinpol 350. Furthermore, increasing the adhesion promoter resin reduced the gloss for inks having Zinpol350 but it did not have any effect on samples containing Glascol LS26. In addition, substrates had serious influence on gloss properties. In other words, gloss quantities for a typical ink that printed on various substrates were different. Results showed that the gloss of samples on PP was more than that of PE. Additionally, Figure 3 showed that samples containing Zinpol 350 had higher print density value rather than samples with Glascol LS26 [4].

Approximately in all samples, the print density values were reduced with increasing adhesion promoter percentage. Using polyester resin decreased gloss and print density but increased resolubility. In addition, samples containing carboxylated acrylic resin showed high gloss. On the other hand, adding the adhesion promoter to ink decreased gloss of samples containing styrene acrylic groups [6].

Table 5 shows overall properties of samples. Coefficient of friction (CoF) and resolubility are important factors for inks especially during high speed printing. As seen from Table 5, the resolubility of Glascol LS26 was very high and an ink with such resolubility has very low block resistance and makes fewer problems in press. On the other hand, resolubility of samples containing Zinpol350 was acceptable but with adding EPDS1300, this value increased which is not favorable. CoF for Zinpol350 was independent of EPDS but for samples containing Glascol LS26, CoF was decreased with increasing the percent of adhesion promoter that could be the cause of higher compatibility of resins.

Table 5: Influence of letdown resin and EPDS percentage on the print properties.

Letdown resin	EPDS (%)	Resolubility (Sec)	Coefficient of Friction
Zinpol 350	0	1	0.92
	3	1.8	0.90
	6	2.8	0.91
Glascol LS26	0	16	1.17
	3	16	0.97
	6	16	0.84

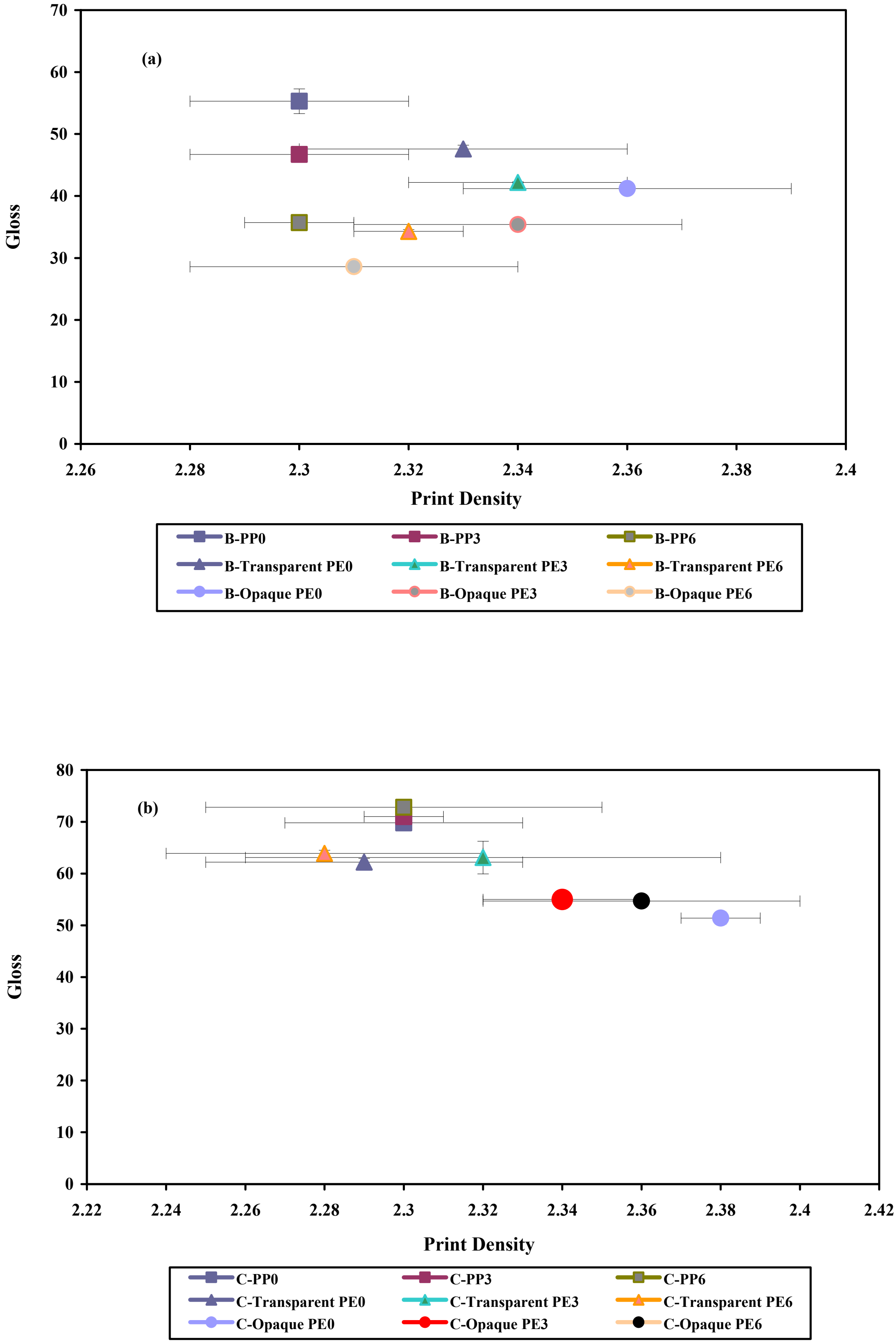

Figure 2: Gloss versus print density plots for three substrates, (a) Zinpol 350, (b) Glascol LS26.

3.3. Print morphology

According to SEM images of printed samples, it can be seen that there were 3-7 micron particles in all samples. These particles can be resulted from weak dispersion ability of letdown resin which can lead to pigment flocculation in ink vehicle. As seen in Figure 4-b, dispersion of Glascol LS26 is better than Zinpol 350. However, by analyzing the morphology of printed surfaces in Figure 3, it was observed that although samples with Zinpol 350 had larger structure on their surfaces which decreases the gloss, but uniformity of the surface was better than other samples. For samples containing Glascol LS26, because of small microstructure and high leveling ability of this resin (Figure 4-b), gloss and adhesion was higher than other samples.

Generally, as shown in Figure 4, adding EPDS 1300 as adhesion promoter did not have any effect on print morphology [10]. It can be concluded that with increasing the percent of adhesion promoter, the surface leveling did not change and because of that, the adhesion did not change. But for samples containing Zinpol 350, as shown in Figure 5 (left section), the morphology changes to small structure with increasing the proportion of EPDS in formulation which scatters more light hence causing the decrease of gloss on printed films.

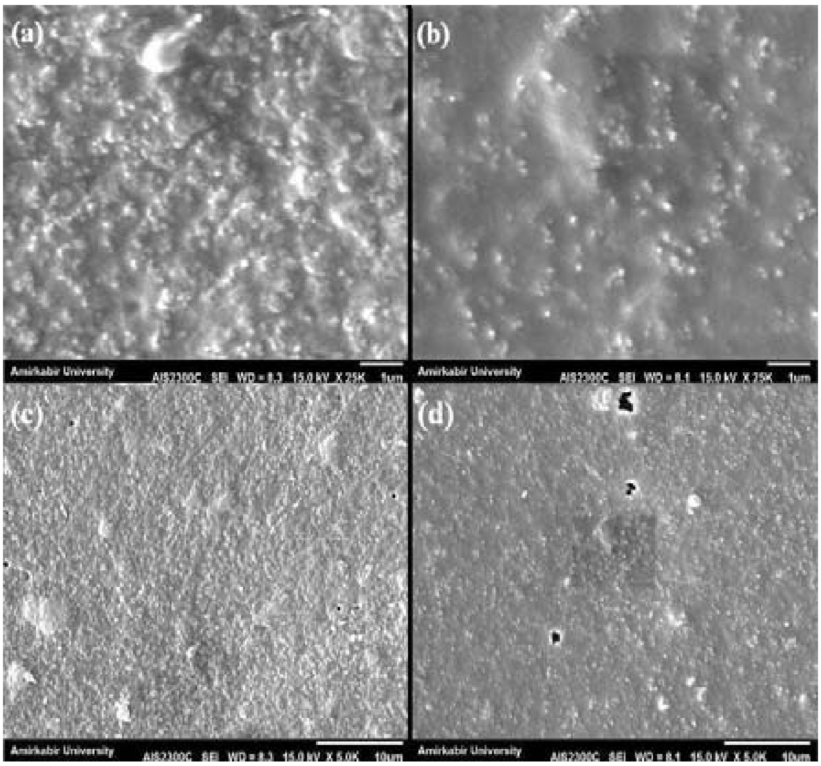

Figure 3: SEM images of printed ink on transparent polyethylene containing: (a) Zinpol 350 (1 μm), (b) Glascol LS26 (1 μm), (c) Zinpol 350 (10 μm) and (d) Glascol LS26 (10 μm) as letdown resin.

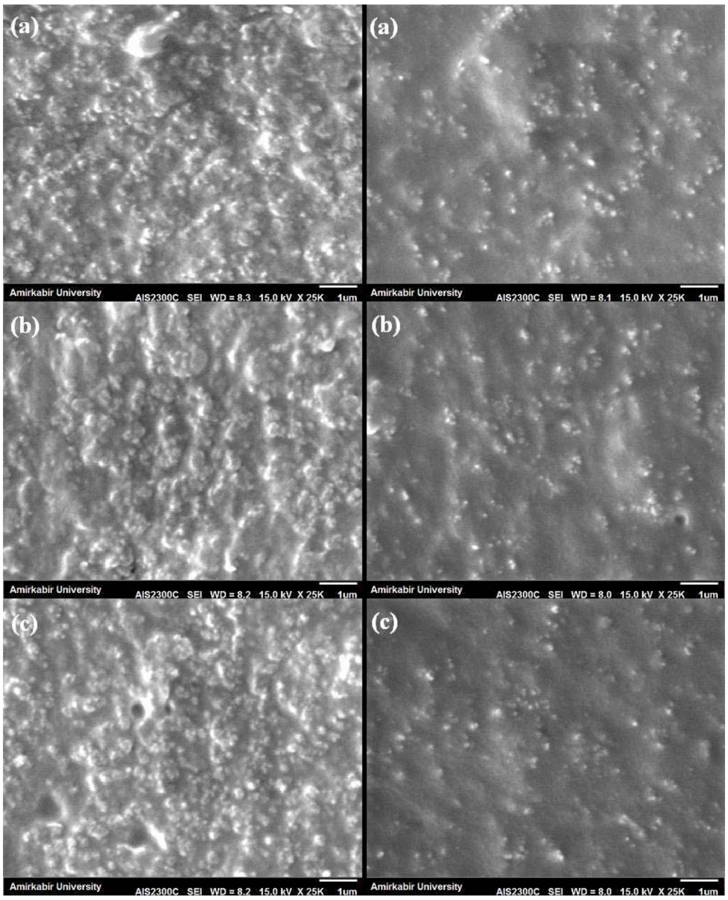

Figure 4: SEM images of printed ink containing Zinpol 350 (left) and Glascol LS26 (right) on transparent polyethylene containing: (a) 0%, (b) 3% and (c) 6% EPDS1300 as adhesion promoter.

4. Conclusions

The effect of changing letdown resin and adhesion promoter content in ink formulation on optical properties and print morphology of three polyolefin printed substrates (PP, transparent and opaque PE) was investigated. The results showed that although the type of substrates had no significant influence on the optical properties and morphology, it affects adhesion and resistance properties of printed films. The types of emulsion resins used in formulation directly influences the morphology of printed films and the amount of ink spread on the substrate, that depends on the resin type, affects its final properties such as adhesion and gloss.

Studies of morphology of printed substrates by electron microscope showed that by increasing the contact area between the substrate and ink due to the high spreading capability of ink on the surface, the adhesion of ink increases up to two times. Moreover, the gloss of samples with more uniform morphology and better spreading on the surface increased because of the decrease in the light scattering of their surfaces. All in all, in order to reach a suitable formulation for water-based printing inks on polyolefin substrates, the influencing parameters must be optimized so as to attain favorable properties.

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5. References

1. A. R. Marrion, The Chemistry and Physics of Coatings, 2nd ed., The Royal Society of Chemistry, Cambridge, UK, 2004. p.8.
2. Y. Gong, B. Q. Huang, X. F. Wei, Comprehensive Research into the influence of Resin on Properties of Environmentally Friendly Water-based Ink, School of Printing and Packaging Engineering, Beijing Institute of Graphic Communication, (2014).
3. F. Garbassi, E. Occhiello and F. Polato, *J. Mater. Sci.,* 22 (1987), 207-212.
4. D. M. Brewis, D. Briggs, In: Industial Adhesion Problems, p.5, Orbiral Press, Oxford (1985)
5. P. Gatnholm, Ch. Bonnerup, E. Wallstorm, Wetting and adhesion of water-borne printing inks on surface-modified polyolefins, *J. Adhes. Sci. Technol.,* 10 (1990), 817-827.
6. P. K. T. Oldring, P. Lam, Waterborne and Solvent Based Acrylics and their end user Applications, John Wiley and Sons, New York, 1998. p.129.
7. A. Tracton, Coatings Technology Handbook, 3rd ed., Taylor & Francis Group, New York, 2006, p.391-394.
8. A. C. I. A. Peters, G. C. Overbeek, T. Annable, Bimodal particle size distribution polymer/oligomer combinations for printing ink applications, *Prog. Org. Coat.*, 38 (2000), 137-150.
9. M. Rentzhog; A. Fogden, Print quality & resistance for water-based flexography on polymer-coated boards: dependence on ink formulation and substrate pretreatment, *Prog. Org. Coat.*, 57 (2006), 183-194.
10. P. Laden; Chemistry and Technology of Water Based Ink; 1st ed., Blackie Academic & Professional, 1997, p.200.
11. L. E. Kincaid; J. D. Meline; G. A. Davis, Cleaner Technologies Substitutes Assessment - A Methodology and Resource Guide, The University of Tennessee, 1996.
12. M. Rentzhog, Water-Based Flexographic Printing on Polymer-Coated Board, PhD Thesis, Royal institute of Technology, Stockholm, Sweden, 2006.
13. BS EN 15386:2007
14. Z. Żołek-Tryznowska, J. Izdebska, M. Tryznowski, *Prog. Org. Coat.*, 2014 DOI: 10.1016/j. porgcoat.