JPMTR 137 | 2005
DOI 10.14622/JPMTR-2005
UDC 544.77-035.67:546.212

Research paper
Received: 2020-06-22
Accepted: 2020-07-07

Optimization of water-based ink formulation based on different NCO : OH ratios of polyurethane dispersion

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Abstract

Due to environmental concerns presently water-based inks are in demand in packaging and label printing, when the application is on paper and paperboard. But these inks are found to be incompatible while printing on a non-porous substrate like the films of polyethylene and polypropylene which are majorly used in the packaging industry for printing. Adhesion as well as optical properties (gloss) of water-based ink deposited onto the polymer film substrate are critical in flexible packaging. Hence the objective is to optimize water-based ink formulation for specific type of binder, its percentage, and percentage of other ingredients such as surfactant and polymer emulsion to achieve the complete adhesion and maximum gloss, which is utmost important for the growth of the water-based ink market in flexible packaging. The design of experiments (mixture model) was conducted to formulate water-based inks by varying the percentages of pigment–binder ratio (resin percentage), surface wetting agent, and polyethylene-based polymer emulsion. Scotch tape qualitative test method was used to measure the adhesion of ink. Adhesion percentage was calculated by analysing the area of ink which remained intact on the substrate. Data was analysed by using the multivariate data analysis method. This model was used to optimize the formulation for complete adhesion of water-based ink on the film substrate. The model explains that complete adhesion of water-based ink on polyethylene substrate takes place at 35.24 % of resin (1 : 1.5 pigment–binder ratio), 1 % of polymer emulsion, and 0.3 % of surfactant. Complete adhesion is observed for 1.35 and 1.4 NCO : OH ratios of polyurethane dispersion. Response surface design was used to find out the effect of binder and surfactant on the gloss of ink. The response surface model explains that surface tension is the dominant parameter for improving the gloss of ink on the substrate. Maximum 80.5 % gloss was observed for higher means at 1.4 NCO : OH ratio of binder and when 0.3 % of substrate wetting agent was used.

Keywords: adhesion, gloss, surface tension, flexography, statistical analysis

1. Introduction

Solvent-based inks have been successfully used in flexography for printing on both absorbent (paper and paper board) and non-absorbent (plastic film) substrates. Environmentally friendly water-based ink (Verspoor, 2005; Saad, 2007; Gu, Li and Zhang, 2013) is an inspiring substitute for the solvent-based inks used in packaging applications. Eco-efficiency analysis of printing inks for flexible packaging has reported that the water-based ink system has a lower overall environmental impact and lower life cycle costs compare to the UV and solvent-based ink system. It also reduces the carbon footprint (Piluso, et al., 2009; BASF Group, 2017). Due to strict environmental rules and regulations industries have started using water-based ink in the packaging field. The water-based ink has been successfully implemented on paper or paperboard substrate which is used in different printing and packaging applications, but these inks are found to be incompatible while printing on a non-porous substrate like the films of polyethylene and polypropylene which are majorly used for packaging printing (Saad, 2007; Gu, Li and Zhang, 2013). High surface tension water-based inks spread poorly on the non-absorbent substrate as they have low surface energy. Poor wetting promotes the adhesion problem of water-based ink on the non-absorbent substrate (Ramirez and Tumolva, 2018). Nowadays, the atmospheric plasma is used to treat the polymer surface to increase the surface energy and hence wettability. Interaction of plasma species with the polymer surface produces chemical groups on the surface for crosslinking and activation (Wolf and

Sparavigna, 2010). Corona treatment is another method used to enhance the surface energy of substrate like polyethylene and hence the adhesion. This can be achieved by grafting appropriate functional groups on the polymer surface, however, corona treatment can damage the physical properties (Izdebska and Thomas, 2015; Ramirez and Tumolva, 2018). Along with these surface treatments up to a certain level, to form good bonding with the ink, modification in ink formulation as well as modification in ink chemistry is a considerable approach in the industry (Chashmejahanbin, et al., 2014; Ramirez and Tumolva, 2018).

Ink adhesion and gloss properties play an important role in flexible packaging as well as in label printing applications. Gloss is also strongly influenced by the surface properties of the substrate and the physical and chemical properties of the ink ingredients which strongly affect the smoothness of ink film (Bohlin, 2013; Ramirez and Tumolva, 2018). The gloss of water-based ink when printed on non-absorbent substrate is majorly influenced by pigment wetting, degree of dispersion, pigment particle size distribution, and the surface tension of water-based system, as these are the influencing parameters for the smoothness of water-based ink film on the non-absorbent surface (Olsson, Yang and Lestelius, 2007).

Experiments were conducted to improve the performance properties of water-based ink. Few of them focused on optimization of ingredients percentage to improve the performance of ink (Rentzhog, 2006; Ramirez and Tumolva, 2018). In some studies, binders were synthesized to improve the performance of ink in terms of gloss, water-resistance, and stability (Yu, Huang and Wei, 2011; Liang and Zhou, 2012; Fang, et al., 2014; Wang, et al., 2016). Few studies focused on the reduction of pigment particle size during the dispersion process which is also one of the influencing parameters for the gloss and performance properties of the ink (Fang, et al., 2010; Tai, et al., 2012; Liang and Zhou, 2012).

To get complete benefit of a pigment both visually and economically, reduction of pigment agglomerates up to the primary pigment particle size is recommended. Visual benefit in terms of color strength depends on the exposed surface area of pigment. Smaller the pigment size, the higher the surface area gets exposed and provides a stronger color (Klein, 2006). Thus, smaller pigment particle size reduces the pigment loading of the formulation (Herbst and Hunger, 2006; Klein, 2006). This reduced amount of pigment loading helps for improving gloss on the non-absorbent substrate.

Studies on pigment dispersion process parameters, their effect on the particle size distribution of pigment, and final performance properties of ink have been in focus from many researchers (Inam, 2010; Inam, Ouattara and Frances, 2011; Abrahão, 2013; Ohenoja, Illikainen, and Niinimäki, 2013; Ohenoja, 2014; Senthilkumar and Akilamudhan, 2014; Simpson, et al., 2015). Studies from Fang, et al. (2010), Ramirez and Tumolva (2018). Inam (2010), Schmidt, et al. (2012) and Hamey (2005) concluded that dispersion process parameters, binders, and surfactants, influence particle size distribution, surface smoothness and the gloss of ink.

Hence optimization of dispersion process parameters as well as optimization of ink formulation needs to be done to improve the performance properties of water-based ink.

Binders, substrate wetting agents and polymer emulsion are the key influencing ingredients for surface tension, adhesion, and gloss of ink. Binder used in ink formulation has a major effect on ink performance properties. Strong demand for the use of eco-friendly products in the packaging industry has increased the demand for use of aqueous polyurethane (PU) binder which has the potential to significantly reduce volatile organic compounds (VOCs) and environmental hazards. NCO : OH ratio of polyurethane dispersion (PUD) alters the urea-urethane groups present in the PU structure (Athawale and Kulkarni, 2010). It also affects the ionic groups and isocyanate groups present in the formulation which are taking part during the reaction (Nanda, et al., 2005; Negim, et al., 2011). Negim, et al. (2011) reported that for increasing NCO : OH ratio, particle size of PUD increases and viscosity decreases. Lei, et al. (2014) also reported that an increase in ionic percentage increases the surface tension of PUD. Thus NCO : OH ratio influences various mechanical, physical, and optical properties of PUD.

There was a little focus on the effect of structural modification such as hard : soft segment ratio, ionic content of PUDs, and their interaction with other ingredients of water-based ink on the printability of ink while printing on non-absorbent substrate. Also, the effect of PUD synthesized from polyester polyol on the performance of water-based ink while printing on non-absorbent substrate is relatively unexplored.

Hence in this research PUD which is synthesized from polyester polyol and for different NCO : OH ratio has been used as one of the parameters during the design of the experiment (DOE).

The objective of this study is to optimize the formulation of water-based ink for specific NCO : OH ratio of polyester-based PUD, pigment–binder ratio, percentage of surfactant and polymer emulsion to get the complete adhesion and maximum gloss of ink on a film substrate.

2. Experimental procedure

Optimized mill base having 28 % pigment loading and 7 % dispersing agent, which provides 128 nm average particle size distribution width was used as a pigment pre-mixture during formulation. The PUDs based on four different NCO : OH ratios, 1.15, 1.27, 1.35, and 1.40, were used in the formulation. The DOE was developed for each NCO : OH ratio of binder and other ingredients of ink. The first part of the experiment consists of optimization of water-based ink in terms of pigment–binder ratio (resin percentage), percentage of wetting agent, and polymer emulsion for four types of resins to get the complete adhesion of ink on the substrate. The multivariate data analysis was conducted to optimize the formulation for each specified resin. Response optimizer was used to fix the pigment–binder ratio (resin percentage) and percentage of polymer emulsion in ink formulation for the adhesion of ink on the non-absorbent substrate.

The second part of the optimization of the formulation is carried out to achieve maximum gloss. Four resins based on different NCO : OH ratio and percentage of the wetting agents were considered as a variable for the DOE. Response surface analysis was carried out to find out the effect of NCO : OH ratios of binder and the effect of substrate wetting agent on the gloss of ink.

2.1 Materials

Stable, homogeneously distributed pigment concentrate consists of rubine red pigment (Sudacolor Red 604 PR 57:1) supplied by Sudarshan Chemical Industry, copolymer with pigment affinic group for improved attachment to the surface of polar pigments as dispersing agent (DISPERBYK-2015) provided by BYK Additives and solution of a polyether-modified polydimethyl siloxane as antifoaming agent (BYK-019) supplied by BYK Additives. The width of the particle size distribution (D90) of pigment paste was 128 nm and total solid loading of 35 % was kept constant throughout the DOE. Thus a constant percentage of pigment, dispersing agent, and antifoaming agent were used in the let-down formulation. Silicon surfactant (BYK-349) supplied by BYK Additives was used as a substrate wetting agent (WA) and deionized (DI) water as a solvent.

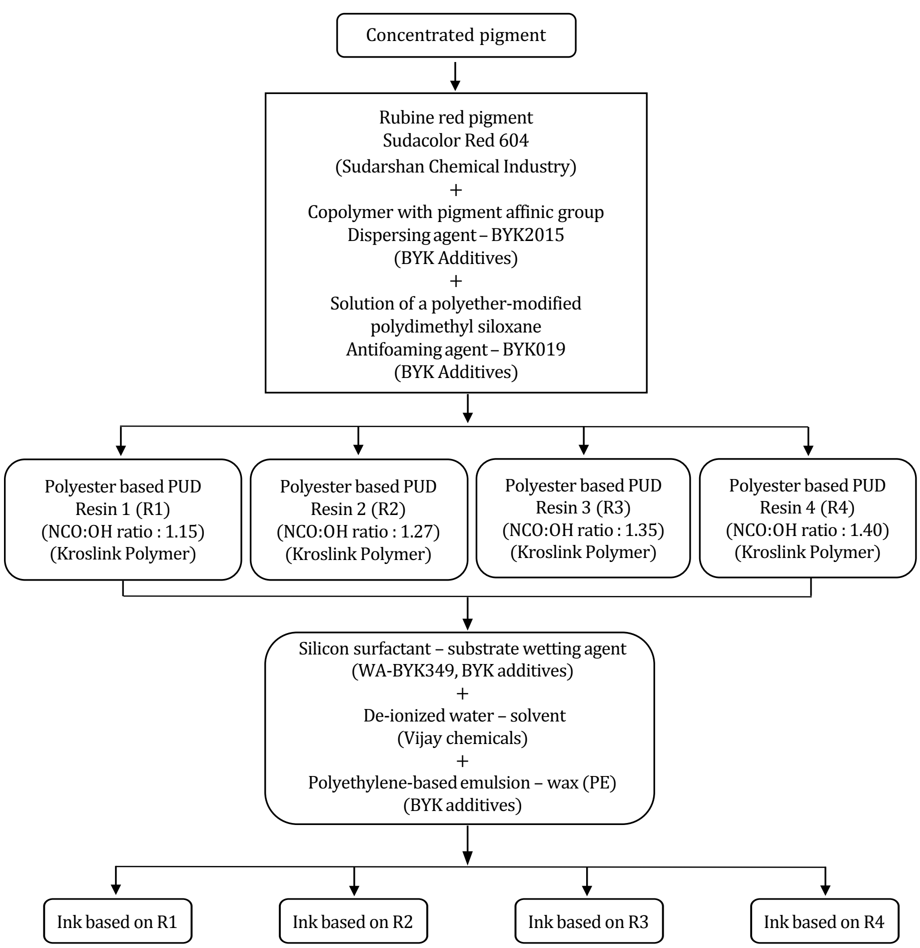


Figure 1: Flowchart for ink ingredients and stepwise addition

In order to improve the scratch resistance, polyethylene-based emulsion (Aquacer 532) provided by BYK Additives was used as a wax. Polyester-based PUD was synthesized by using isophorone diisocyanate, polyethylene-based polyol, and dimethyl propionic acid (DMPA) by the pre-polymerization method. Polyurethane dispersions were provided by Kroslink polymer. Four PUDs based on different NCO : OH ratios, 1.15 (R1), 1.27 (R2), 1.35 (R3), and 1.40 (R4), were used as one of the variables of DOE. The flexible substrate chosen was low density polyethylene (LDPE, thickness: 40 μm) provided by the Parakh Agro company. Figure 1 shows the flowchart for ink ingredients and their stepwise addition which is self-explanatory.

2.2 Characterization

Fourier transform infrared (FTIR) spectra of samples were recorded by using SHIMADZU IR spectrometer in the wavenumber range of 400–4 000 cm^{-1}. Particle size distribution (PSD) measurements of PUD and ink samples were carried out using Malvern Particle Size Analyser, Zetasizer Nano-S90 model. The viscosity of PUD was measured with a rotational viscometer Anton Paar Physica MCR101. The glass transition temperatures (T_g) were determined on Pyris controlled PerkinElmer DSC 4000 Thermogravimetric Analyzer under the continuous purge of nitrogen at 20 ml/min. The measurements were carried out in the temperature range of −100 °C to 100 °C. Field emission scanning electron microscope (SEM) Nova NanoSEM 450 equipped with energy dispersive X-ray spectrometer (EDS) BRUKER, XFlash 6130 was used to investigate the microstructure and elemental composition of materials. Solid content of PUD and pigment dispersion paste was determined as per ISO 124:1997 standard procedure by using hot air oven (International Organization for Standardization, 1997). Viscosity measurements of the ink were performed using Brookfield DV-I viscometer, at a shear rate of 100 s^{-1} at 25 °C. The pH of ink was measured by Hanna pH meter HI991001P with 0.01 pH resolution and an accuracy of ±0.05 pH. A quantitative standard test method for specular gloss defined by ASTM (ASTM International, 2018a) was used in the second part of experiment. Gloss was measured by Rhopoint Novo-Gloss meter. The standard measurement geometry of the gloss meter is 20°, 60°, or 85° depending on the test sample. In this experiment, the medium gloss range (60° angle) was used to determine the gloss values.

2.3 Design of experiment

A mixture experiment model of a DOE is a special class of response surface experiments in which the product is made up of several components or ingredients. In mixture design, the product was formed by the mixture of product ingredients in different proportions. Product quality or performance of the product (response) is dependent on the relative proportions of the components. In this experiment performance of ink depends upon the relative proportion of ingredients such as pigment–binder ratio (resin percentage), wetting agent, and polymer emulsion. If we increase the percentage of one ingredient it reduces the percentage of other ingredients, which means the final performance properties of inks such as adhesion, surface tension, gloss and stability depend upon the relative proportion of each ingredient. Mixture design model provides the interaction of each ingredient and optimizes the percentage of ingredients by considering their interaction with each other.

The Minitab 17 statistical software was used to statistically analyze the data and for the prediction of response.

Table 1: Variables and levels for DOE

Variables	Level-1	Level-2
P : B ratio	1 : 1.3	1 : 1.5
WA (%)	0.2	0.3
PE (%)	0.5	1.0

Table 2: Design of experiment for analysis of adhesion for 24 formulations

Formul. no.	Resin (%)	WA (%)	PE (%)	Water (%)
1	30.56	0.2	0.5	36.87
2	30.56	0.2	0.5	36.87
3	30.56	0.2	0.5	36.87
4	30.56	0.3	0.5	36.77
5	30.56	0.3	0.5	36.77
6	30.56	0.3	0.5	36.77
7	30.56	0.2	1.0	36.37
8	30.56	0.2	1.0	36.37
9	30.56	0.2	1.0	36.37
10	30.56	0.3	1.0	36.27
11	30.56	0.3	1.0	36.27
12	30.56	0.3	1.0	36.27
13	35.24	0.2	0.5	32.19
14	35.24	0.2	0.5	32.19
15	35.24	0.2	0.5	32.19
16	35.24	0.3	0.5	32.09
17	35.24	0.3	0.5	32.09
18	35.24	0.3	0.5	32.09
19	35.24	0.2	1.0	31.69
20	35.24	0.2	1.0	31.69
21	35.24	0.2	1.0	31.69
22	35.24	0.3	1.0	31.59
23	35.24	0.3	1.0	31.59
24	35.24	0.3	1.0	31.59

The DOE for ink formulation involves two levels of each: pigment to binder ratio (P : B) expressed also as resin percentage, wetting agent (WA), and polymer emulsion (PE) as shown in Table 1. The DOE was repeated for four resins to determine the performance of different properties of a resin with other ink ingredients. The DOE is as shown in Table 2, which considers the total of 24 formulations for one resin. These 24 formulations were repeated for four resins, thus a total of 96 formulations were evaluated for adhesion of ink.

In this experiment, pigment paste was used as 31.87 % to get 9 ± 0.5 % pigment loading in let-down formulation, which maintains the constant pigment loading, constant percentage of a dispersing agent, and an antifoaming agent in the let-down formulation designed by the mixture model of the DOE.

The second part of the experiment considers four PUD resins based on different NCO : OH ratios and two percentages of the wetting agent as a variable to find out their effect on gloss and optimize the formulation for highest gloss. The values for both variables are as shown in Table 3.

Table 3: Design of experiment for gloss

Variables	Level-1	Level-2	Level-3	Level-4
PUD with different NCO : OH ratio	1.16	1.27	1.35	1.40
WA (%)	0.5	0.3	–	–

2.4 Surface energy

The surface energy of the LDPE substrates was determined from the contact angle measurements. Three liquids (purified deionized water supplied by Vijay Chemicals, formamide, and glycerol both supplied by Thermo Fisher Scientific) of known surface tension i.e. surface energy γ, with dispersive component γ_d and polar component γ_p of the liquids (Table 4) were used, and the contact angle of these liquids on LDPE films was measured by using the Holmarc contact angle meter.

Table 4: Surface energy, polar and dispersive component of test liquids

Sample	γ (mJ/m^2)	γ_d (mJ/m^2)	γ_p (mJ/m^2)
Water	72.8	21.8	51.0
Formamide	58.2	39.6	18.6
Glycerol	63.4	37.0	26.4

Surface energy, dispersive components, and polar components of LDPE substrates were calculated by using Fowke's model. The theoretical basis of this is the Young–Dupre equation. In this model, as shown in Equation [1], the work of adhesion (adhesion energy) W_a is expressed in terms of the dispersive and polar components of the surface energy (Carré, 2007; Izdebska and Thomas, 2015).

$$\gamma_l (1 + \cos \theta) = 2[(\gamma_{ld} \cdot \gamma_{sd})^{1/2} + (\gamma_{lp} \cdot \gamma_{sp})^{1/2}] \quad [1]$$

where γ_l is the surface tension of the ink, θ is the angle made by ink with the surface of the substrate, γ_{ld} and γ_{sd} are dispersive components of the ink and solid substrate, and the γ_{lp} and γ_{sp} are polar components of the ink and solid substrate, respectively.

The interfacial tension γ_{sl}, work of adhesion W_a, and spreading coefficient S have been calculated using Equations [2] to [4]:

$$\gamma_{sl} = \gamma_s - \gamma_l (\cos \theta) \quad [2]$$

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \quad [3]$$

$$S = \gamma_s - \gamma_l - \gamma_{sl} \quad [4]$$

where γ_s is the surface energy of the substrate.

Surface tension of the ink was measured by using a ring tensiometer. The interfacial surface tension between ink formulated from PUD which was based on different NCO : OH ratio and LDPE substrate were calculated by the Young equation.

A stirrer with a maximum speed of 2 600 rpm was used for mixing of all the ink ingredients. Each let-down mixture was stirred for 30 minutes. Automatic film applicator LLOYD model SM 102 and barcoater (number: 0, thickness: 4 µm) was used for a drawdown of each formulation onto the substrate. Drawdowns were taken at 65 mm/s speed.

2.5 Adhesion of ink

Adhesion of water-based ink was measured by using the ASTM adhesion method (ASTM International, 2017). Adhesion test method F2252 / F2252M (ASTM International, 2018b) was performed using a standard 3M #610 Scotch tape, 25–38 mm (1–1.5 inch) wide, and manually pulling off the tape to determine the degree of ink adhesion or ink removal from the substrate.

For evaluation the glass slab which is marked with a one-inch square area (25.4 mm × 25.4 mm) divided into 16 squares was used. As the grid was applied on the glass slab it did not affect the printed ink layer of the sample. The peeling off the Scotch tape from the ink coated substrate was done as per the standard method. The peeled tape was pasted on the non-printed area of the substrate. The marked grid of glass slab was kept on the peeled tape and each area of the grid was examined to investigate the removal of ink through an optical microscope. The number of squares which remain intact provides the total adhesion of ink on the substrate. The percentage of adhesion was calculated by using Equation [5].

$$\text{Adhesion of ink} = \frac{\text{Number of intact squares}}{\text{Number of total squares}} \cdot 100 \ (\%) \quad [5]$$

Grading A to E was used based on an intact percentage. Reference for intact percentage and grading is as follows:

A – 100 % adhesion and 0 % removal of an ink,
B – 75 % adhesion and 25 % removal of an ink,
C – 50 % adhesion and 50 % removal of an ink,
D – 25 % adhesion and 75 % removal of an ink,
E – 0 % adhesion and 100 % removal of an ink.

2.6 Printed samples preparation

The formulated water-based inks were printed on a LDPE substrate by the drawdown method. After printing, samples were dried using air blower for 5–10 s, and then allowed to dry for 24 h to cure the ink. Ten drawdowns for each condition were printed. Thus, a total of 1 080 samples were printed. The density value D of each sample was measured at 6 different places and the sample which has minimum deviation (D = 0.85 ± 0.5) was selected for sampling. Three samples having minimum deviation were selected as a sample size for each condition of the mixture model. A total of 288 samples were selected for all four types of resin models.

3. Results and discussion

3.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was used to analyse the functional group of PUD. Figure 2 shows the FTIR of PUD used during formulation.

The FTIR spectra of all the PUDs showed characteristic absorption band between 3 457 cm^{-1} to 3 352 cm^{-1} indicating N-H stretching vibrations. The absorption bands observed at 2 952 cm^{-1} and 2 950 cm^{-1} are associated with C-H stretching of the CH_2 group. The band at 1718 cm^{-1} to 1709 cm^{-1} corresponds to C=O stretching from ester and urethane groups. According to the characteristic peaks, C=O (1718 cm^{-1} to 1709 cm^{-1}) and N=H (1532 cm^{-1} to 1530 cm^{-1}), the formation of the urethane group (-NHCOO-) was confirmed. Slight transmittance at 2 270 cm^{-1} shows the presence of a slight percentage of NCO. The presence of the NCO band at 2 355 cm^{-1} confirms the presence of free urethane as a higher percentage of NCO : OH ratio is used.

3.2 Characterization of PUDs

Table 5 shows the characteristics of the PUDs (binders) prepared by using different NCO : OH ratios, marked from R1 to R4, used for the DOE.

Table 5: Physical properties of PUDs for different NCO : OH ratio and constant molar ratio of PEG and DMPA

Variables	R1	R2	R3	R4
NCO : OH ratio	1 : 1.15	1 : 1.27	1 : 1.35	1 : 1.40
Avg. particle size (nm)	29.02	47.88	64.98	65.63
Width of PSD (nm)	57.30	59.50	71.90	80.00
Viscosity at 30 °C (mPa·s)	734	665	520	494
Solids (mass fraction, %)	36.04	35.95	36.95	36.16

3.3 Effect of NCO : OH ratio on T_g of PUD

The result of differential scanning calorimetry (DSC) measurement of PUD with NCO : OH ratio of 1.4 is shown in Figure 3. The results of retrieved T_g of PUDs for different NCO : OH ratios are shown in Table 6. It was observed that T_g of PUD increases from −16.40 °C to −8.35 °C as NCO : OH ratio increases from 1.16 to 1.40. The results are in line with previous research (Negim, et al., 2011).

The higher percentage of NCO contributes to the formation of urea groups. The T_g value is slightly higher for 1.4 NCO : OH ratio due to an increased percentage of hard segments. Increased hard segment provides stronger physical crosslinking through hydrogen bonding and improve the adhesion of water-based ink on the non-absorbent substrate such as LDPE.

Table 6: Glass transition temperature of PUDs for different NCO : OH ratios

NCO : OH ratio	T_g (°C)
1.15	−16.40
1.27	−11.58
1.35	−9.40
1.40	−8.35

3.4 Scanning electron microscope and energy-dispersive X-ray results

Figure 4 shows SEM and EDS results of the LDPE surface. The EDS analysis shows the presence of nitrogen and oxygen groups on the surface of LDPE material. Strong bond formation observed with these groups may be explained with the urea and urethane group present in the PUD. Free NCO present in the dispersion will help to form a stronger bond with the substrate.

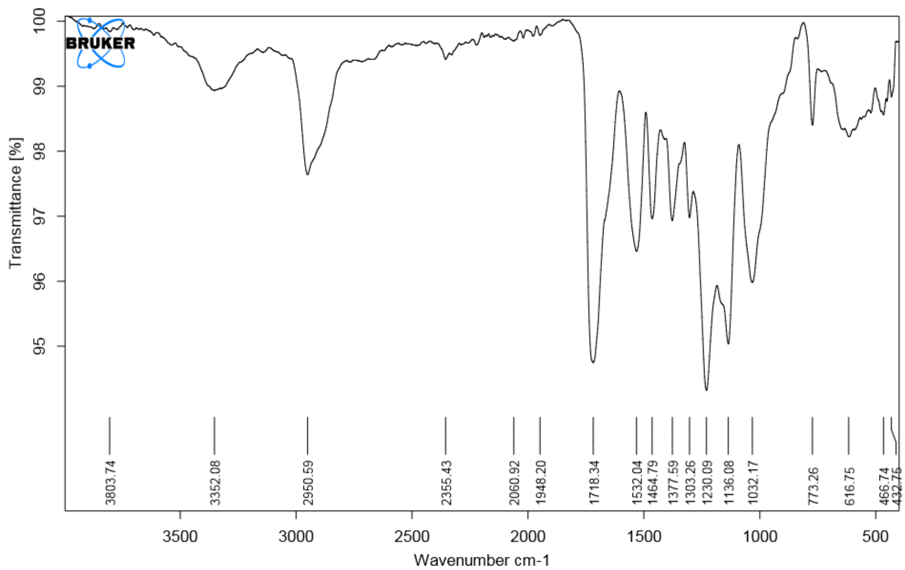


Figure 2: The FTIR spectrum of PUD

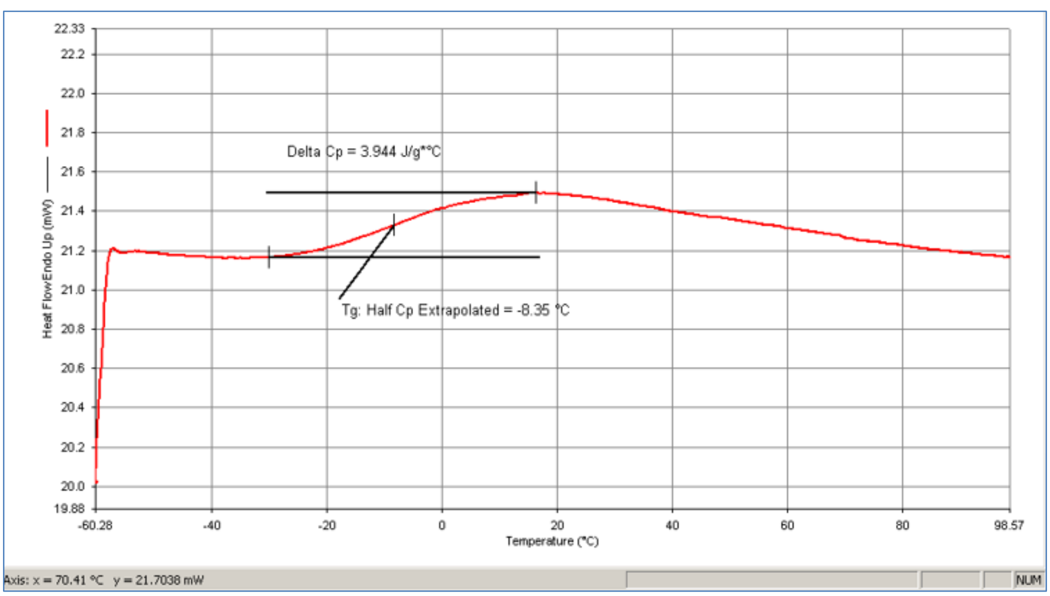
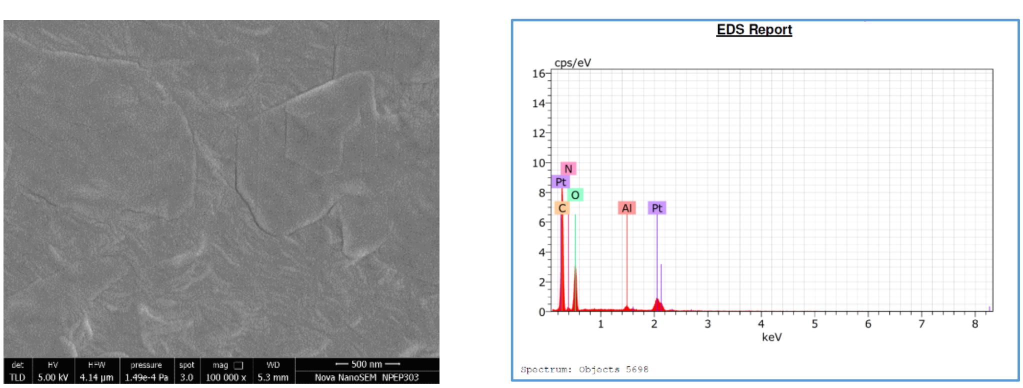


Figure 3: The DSC curve of PUD at 1.4 NCO : OH ratio



a) b)

Figure 4: The LDPE surface: (a) SEM picture, and (b) EDS analysis results

3.5 Surface energy of LDPE film

Table 7 shows the average value of the polar component, disperse component, and surface energy of LDPE film calculated by using three liquids.

Table 7: Surface energy, dispersive and polar components of LDPE non-absorbent film

Sample	γ_s (mJ/m^2)	γ_{sd} (mJ/m^2)	γ_{sp} (mJ/m^2)
LDPE	39.63	36.44	3.19

4. Statistical analysis

4.1 Simplex design plot

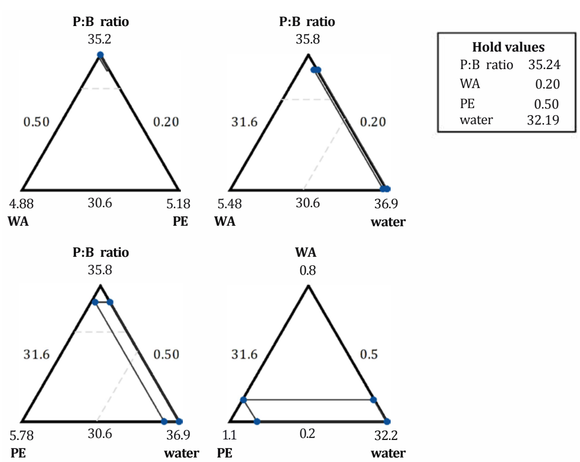


Figure 5: Simplex design plots in amounts for P : B ratio, PE, WA and water

A simplex design plot is used to visualize the mixture design space or a slice of the design space for more than three components. Minitab software plots the design points on the triangular axes as shown in Figure 5. The vertices of the triangle show the three pure mixtures for each component (PE, P : B ratio, WA, and water). Three binary blends are found at the midpoint of each edge of the triangle. Inside the triangle, blends are for three components but not in equal proportion. The blend at one centre point (or centroid) represents the proportions of all three components.

4.2 Statistical analysis for adhesion of water-based ink

Table 8 presents the analysis of variance (ANOVA) for the adhesion test and regression mixture model for PUD resin based on 1.16 NCO : OH ratio, marked as WB_AD_R1.

The ANOVA Table 8 helps to understand the significance of a ratio of ink ingredients for the adhesion of ink on the non-absorbent substrate. For mixture design the main terms that represent the three factors are P : B ratio, WA, and PE, among that the magnitude of the coefficient indicates that for P : B ratio (44) provides adhesion with higher acceptance levels. The individual responses of WA (−11350) and PE (−1751) have no impact on the adhesion. Positive coefficients for two blend mixtures such as P : B ratio with WA, P : B ratio with PE, and PE with WA indicate that two components of each blend act synergistically with each other.

The significance of the ratio of elements is defined by the nearness of the *p*-values of a parameter to the defined significance level. If *p*-value is lower than 0.05, the ratio is significant for the adhesion of ink. From the ANOVA Table 8, it is observed that P : B ratio with the WA and P : B ratio with PE both have *p*-value less than 0.05, which means these ratios are significant for the adhesion of ink on the non-absorbent substrate. Significance of P : B ratio with PE is higher than that of P : B ratio with WA ratio. Ratio of WA and PE has a *p*-value above 0.05 which indicates that ratio is having less influence for the adhesion. Also, the model has an *R*-squared value of 97.96 %, which indicates a good data fit without excluding insignificant terms.

Table 9 shows ANOVA and the magnitude of coefficients for resin, PE, and WA for the ink formulated from 1.4 NCO : OH ratio, marked as WB_AD_R4. For higher NCO : OH ratio even though the NCO terminated polymer chain is dispersed in water, free NCO is available in the dispersion. This free NCO tends to crosslink with the surface as well as with another ingredient in the presence of water and this will promote the adhesion of ink on a non-absorbent surface. Thus water-based inks which are formulated from PU resin which have higher NCO : OH ratio i.e. 1.4 in this experiment provide better interaction with other ingredients of ink and thus complete adhesion of ink on LDPE substrate.

4.3 Histogram and plot of residual

Figure 6a shows the normal probability plot for the adhesion response obtained from the DOE conducted for binder R1. Normal probability plot determines how well data follow a specific distribution. The degree of fit is indicated by the degree to which the data points follow the fitted line.

Figure 6b shows the histogram of the adhesion response. This is the distribution of the residuals for all observations. The histogram helps to understand the spread, variation, and shape of the distribution and if any unusual values are present in data. Data follows the normal distribution plot with a mean value of the adhesion response of 76.93 % and a standard deviation of 4.04 %.

Table 8: Statistical analysis for WB_AD_R1 (resin based on 1.15 NCO : OH ratio)
Regression for mixtures: WB_AD_R1 versus P : B ratio, WA, PE, water
Estimated regression for WB_AD_R1 (component proportions)

Term	Coef.	SE coef.	*t*-test	*p*-value	VIF
P : B ratio	44	14.7	*	*	1 920.3
WA	−11 350	3 183.1	*	*	5 360.1
PE	−1 751	655.9	*	*	2 188.5
Water	84	13.8	*	*	1 820.7
P : B ratio * WA	26 548	6 454.6	4.11	0.001	5 165.6
P : B ratio * PE	5 356	1 290.9	4.15	0.001	1 986.8
WA * PE	28 779	60 414.6	0.48	0.640	260.0

S = 0.80 PRESS = 21.52
R-sq = 98.43 % *R*-sq(pred.) = 96.87 % *R*-sq(adj.) = 97.88 %

Analysis of variance for WB_AD_R1 (component proportions)

Source	DF	Seq. *SS*	Adj. *SS*	Adj. *MS*	*F*-value	*p*-value
Regression	6	676.90	676.90	112.82	177.90	0.000
Linear	3	655.07	41.43	13.81	21.74	0.000
Quadratic	3	21.83	21.83	7.27	11.45	0.001
P : B ratio * WA	1	10.75	10.75	10.75	16.92	0.001
P : B ratio * PE	1	10.93	10.93	10.93	17.21	0.001
WA * PE	1	0.14	0.14	0.14	0.23	0.640
Residual error	17	10.80	11.00	0.63		
Lack-of-fit	1	2.73	2.73	2.73	5.42	0.033
Pure error	16	8.07	8.07	0.50		
Total	23	687.70				

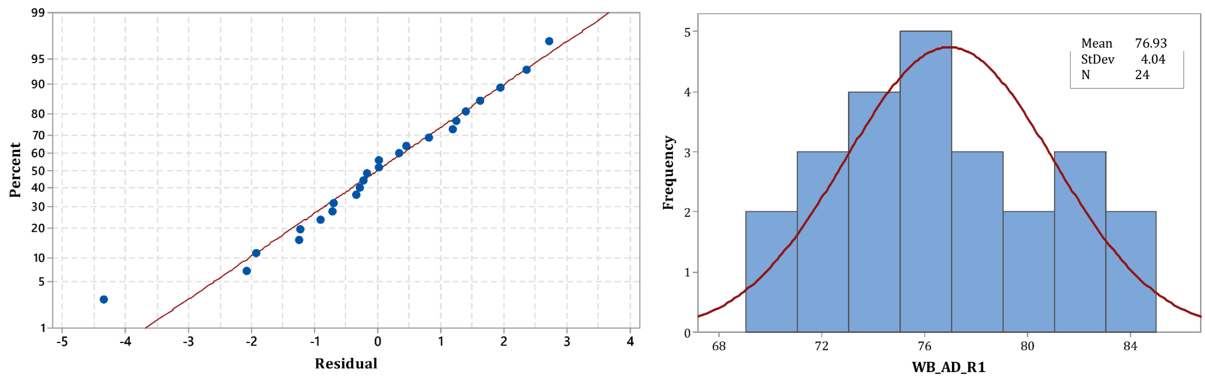
Table 9: Statistical analysis for WB_AD_R4 (resin based on 1.40 NCO : OH ratio)
Regression for mixtures: WB_AD_R4 versus P : B ratio, WA, PE, water
Estimated regression for WB_AD_R4 (component proportions)

Term	Coef.	SE coef.	*t*-test	*p*-value	VIF
P : B ratio	63	6.5	*	*	1 920.3
WA	−2 404	1 410.3	*	*	5 360.1
PE	−3 036	290.6	*	*	2 188.5
Water	95	6.1	*	*	1 820.7
P : B ratio * WA	8 678	2 859.8	3.03	0.007	5 165.6
P : B ratio * PE	7 720	572.0	13.50	0.000	1 986.8
WA * PE	8 510	26 768.8	0.32	0.754	260.0

S = 0.35 PRESS = 4.23
R-sq = 99.47 % *R*-sq(pred.) = 98.94 % *R*-sq(adj.) = 99.28 %

Analysis of variance for WB_AD_R4 (component proportions)

Source	DF	Seq. SS	Adj. SS	Adj. MS	*F*-value	*p*-value
Regression	6	394.900	394.970	65.810	527.7100	0.000
Linear	3	371.000	23.700	7.900	63.6500	0.000
Quadratic	3	23.900	23.880	7.960	63.8200	0.000
P : B ratio * WA	1	1.100	1.148	1.150	9.2100	0.007
P : B ratio * PE	1	22.700	22.720	22.720	182.1600	0.000
WA * PE	1	0.013	0.013	0.013	0.1000	0.754
Residual error	17	17.000	2.120	2.120	0.1247	
Lack-of-fit	1	0.600	0.550	0.550	5.6800	0.030
Pure error	16	1.600	1.560	0.098		
Total	23	397.000				



a) b)

Figure 6: Response of WB_AD_R1 formulation: (a) normal probability plot, and (b) histogram of the adhesion

4.4 Main effect plot and interaction plot

The main effect plot (Figure 7a) shows the effect of ingredients on the adhesion of water-based ink. This plot considers the data means at the various levels of each factor, with a reference line drawn at the grand mean of the response data. Main effect plot shows that the adhesion of water-based ink on the non-absorbent substrate is obtained for a higher level of P : B ratio (resin percentage), WA, and PE.

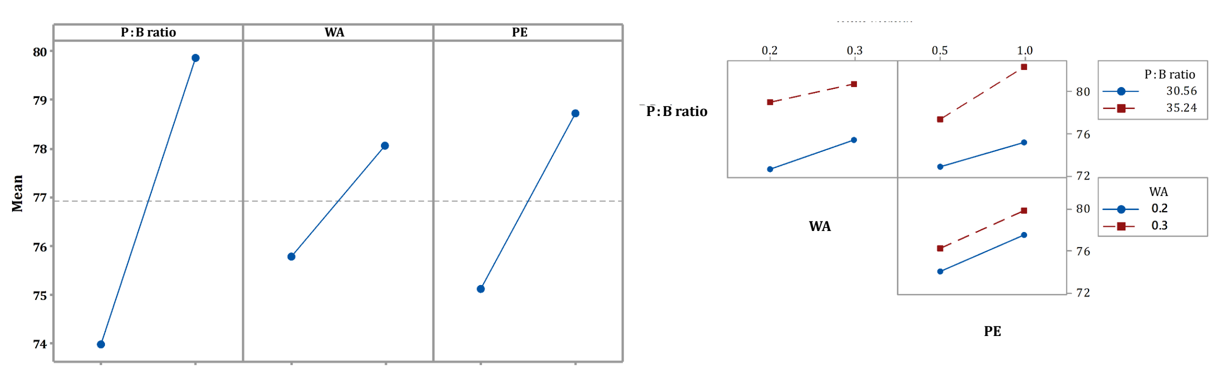
Figure 7b shows the interaction plot for all three ingredients. An interaction plot is a plot of means for each level of a factor with the level of a second factor held constant. Interaction plots are useful for judging the presence of interaction. Interaction is present when the response at a factor level depends upon the level(s) of other factors. Parallel lines in an interaction plot indicate no interaction. The greater the departure of the lines from the parallel state, the higher the degree of interaction. Figure 7b shows that interaction takes place between P : B ratio with WA, P : B ratio with PE, and WE with PE as lines are not parallel. Interaction between resins with WA is more acceptable than the interaction between resin and PE for the adhesion of ink.

Overall, all regression mixture model explains the significance of P : B ratio (resin percentage), a blend of resin with WA, resin with PE for the adhesion of ink on the non-absorbent surface. From the estimated regression coefficient of all four models, it is observed that the magnitude of resin and magnitude of a blend of resin with PE increase for increasing NCO : OH ratio of resin. For the increasing value of NCO : OH ratio, more interaction is observed between resin and polymer emulsion which is observed from the magnitude of these coefficients.

4.5 Mixture contour plot

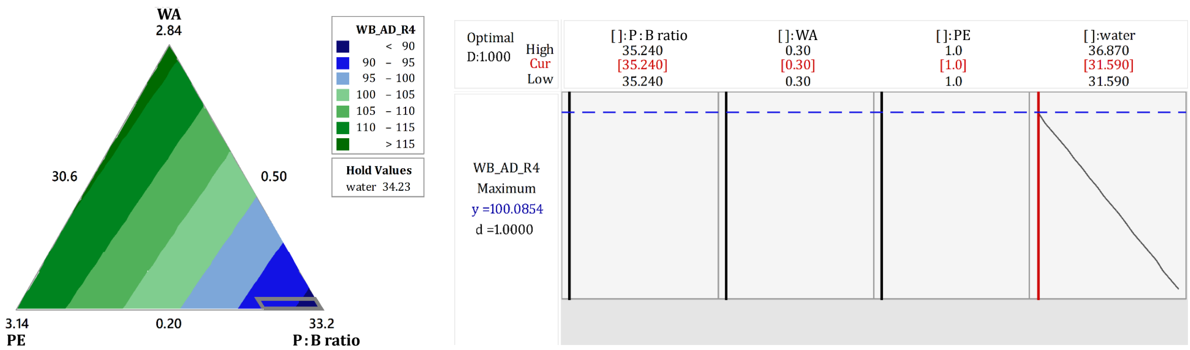
Figure 8a shows the contour plot for the mixture model for R4 resin. A contour plot provides a two-dimensional view where all points that have the same response are connected to produce contour lines of constant response.

The response optimizer uses the model equation to optimize the result. Response optimizer shown in Figure 8b predicts that complete adhesion of water-based ink on LDPE substrate will be observed when NCO : OH ratio of the PU resin is 1.4. At this NCO : OH



a) b)

Figure 7: The effect of ingredients in WB_AD_R1: (a) main effect plot, and (b) interaction plot



a) *b)*

Figure 8: Component amounts in WB_AD_R4: (a) mixture contour plot, and (b) response optimizer

ratio, 35.24 % of resin, 1 % of polymer emulsion, and 0.3 % of surfactant provides the complete adhesion of water-based ink on LDPE substrate. Table 10 shows the values obtained from the response optimizer.

Table 10: Statistical analysis for WB_AD_R4 response optimization

Goal	Lower	Target	Upper	Weight	Import
Maximum	80	100	100	1	1

Predicted responses

Components	
P:B ratio	35.24
WA	0.30
PE	1.00
Water	31.59

WB_AD_R4 = 100.00

5. Effect of NCO:OH ratio on the surface tension of water-based ink

The surface tension of four water-based ink formulated based on R1, R2, R3, and R4 resin with a constant percentage of WA as 0.3 % and PE as 1 % were measured by using a ring tensiometer. Figure 9 shows the effect of NCO:OH ratio of PUD on the surface tension of the ink.

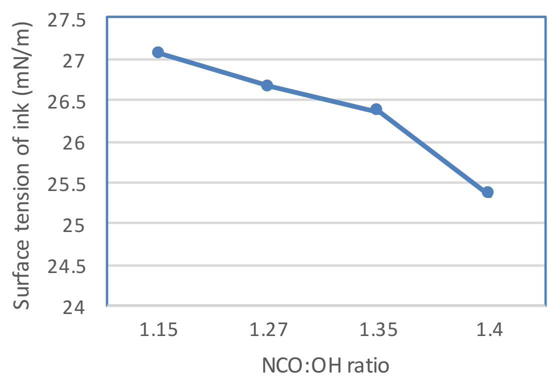


Figure 9: Surface tension of ink for different NCO:OH ratios

The surface tension values of ink formulated from different NCO:OH ratios were analyzed. Four PUDs based on four NCO:OH ratio, 1.15, 1.27, 1.35, and 1.4, have a constant molar ratio of polyester glycol and DMPA. When NCO:OH ratio is higher, the percentage of NCO increases while the amount of hydrophilic carboxyl group contents reduces. Reduced amount in ionic groups reduces polar group element of PUD; ultimately surface tension of ink gets reduced for higher NCO:OH molar ratio.

The interfacial tension between water-based ink and substrate plays a significant role in the wetting of the substrate. The higher interfacial tension produces uneven surface performance. Table 11 shows the values for the interfacial surface tension of ink and LDPE

Table 11: Interfacial surface tension, work of adhesion and coefficient of spreading for inks made from four binders

Substrate	Ink based on PUD	θ (°)	Cos θ	γ_s (mN/m)	γ_l (mN/m)	γ_{sl} (mN/m)	W_a (mJ/m²)	S (mJ/m²)
LDPE	R1	44.12	0.72	39.63	27.06	20.20	46.49	−7.63
	R2	41.00	0.75	39.63	26.65	19.59	46.69	−6.61
	R3	38.25	0.78	39.63	26.35	18.98	47.00	−5.70
	R4	30.37	0.86	39.63	25.35	17.76	47.22	−3.48

film. It was observed that when NCO : OH is higher, the hydroxyl group percentage is less, which reduces the interfacial surface tension between ink and film and allows the ink to wet the LDPE substrate easily and provide a uniform surface of ink on LDPE film.

The interaction between the ink and the substrate plays a major role in print quality. During the transfer of ink from anilox cylinder to image carrier and from the image carrier to the substrate, how the ink behaves, is a significant aspect for printability. The spreading/wetting of ink over the substrate leads to a reduction in voids, which also helps to improve the adhesion of ink over the substrate. Poor wetting causes uneven spreading of ink over the substrate which provides uneven reflectance from the printed surface. This also leads to poor adhesion and hence less scratch resistance and abrasion resistance. The γ_{sl}, W_a, and S have been calculated using the Equations [2] to [4].

The W_a is the work required to separate the interface between ink and substrates. The greater adhesion energy is a decisive parameter to get good adhesion between liquid and substrate.

Table 11 shows the lower contact angle is achieved by water-based ink on LDPE substrate when NCO : OH ratio is high i.e. 1.4. The lower value of the contact angle provides a higher spreading of ink for the substrate. The high surface energy of the LDPE substrates increases the wettability as spreading or wettability is directly proportional to the difference in the surface energy of the substrate and water-based ink. Improved wettability improves the ability of the substrate to bind with the water-based ink. The higher W_a on the LDPE substrate from the ink which is formulated from PUD of NCO : OH ratio 1.4, indicates a higher adhesion between the ink and the substrate. Negative value S shows that the spreading does not occur impulsively. The higher is the negative magnitude of S, the lower is the spreading for the corresponding combination of ink and substrate. The water-based ink formulated from PUD of 1.4 NCO : OH ratio provides a very small negative coefficient which is close to zero, hence provides spreading but not spontaneously. Also, work done at this NCO : OH ratio is also high to get the adhesion between ink and substrate.

6. Statistical analysis for gloss of water-based ink

6.1 Gloss of water-based ink on LDPE substrate

Table 12 shows the formulation of water-based ink for the different DOE, measured at 60° angles of light reflection in the second part of experiment.

Table 12: Ink formulation for design of experiment for gloss

Sample	NCO : OH ratio	WA (%)
1	1.15	0.2
4	1.15	0.3
7	1.27	0.2
10	1.27	0.3
13	1.35	0.2
16	1.35	0.3
19	1.40	0.2
22	1.40	0.3

Table 13 shows the output from two way ANOVA table summarizing the linear term, the squared term, and the interaction for gloss. The small p-value for the linear term of NCO : OH ratio and WA shows that they are linearly affecting gloss of ink. The small p-values for the square term of NCO : OH ratio and the interaction of NCO : OH ratio and WA suggest that there is the curvature in the response surface. The F-values from the model indicate that their linear significance for NCO : OH ratio and WA is higher than the quadratic significance of the interaction between both factors. The model has an R-squared value of 91.28 %, which indicates almost perfect data fit of the model.

6.2 Histogram and residual plot

Figure 10 shows the normal distribution plot and histogram of data with mean of 73.3 and standard deviation of 4.7.

6.3 Main effect and interaction plot for gloss

Figure 11 shows the main effect plot and interaction plot for different NCO : OH ratios and wetting agent percentage. The percentage of wetting agent provides linear relation for the gloss of ink. NCO : OH ratio is affecting by the different rates on the response gloss. Different rates of response interpreted that different surface tension of ink due to NCO : OH ratio and particle size distribution of binder for different NCO : OH ratios are simultaneously affecting with substrate wetting agent. This leads to the uneven response rate for the gloss of ink.

A gloss of ink is majorly dependent upon the uniform and smoothness of the ink layer on the substrate. Reduced surface tension provides the spreading of ink on substrate uniformly while a narrow particle size distribution helps to provide a smoother surface on film.

From interaction plot (Figure 11b) it is observed that NCO : OH ratio of 1.35 and 0.3 % of wetting agent provide slightly higher gloss means (higher by 0.63 %).

Table 13: Response surface regression for gloss

Response surface regression: gloss versus NCO : OH and WA

Stepwise selection of terms α to enter = 0.15, α to remove = 0.15

Analysis of variance for gloss

Source	DF	Adj. SS	Adj. MS	*F*-value	*p*-value
Model	4	454.6	113.6	49.7	0.000
Linear	2	410.7	205.3	89.8	0.000
NCO : OH	1	228.8	228.8	100.0	0.000
WA	1	181.9	181.9	79.6	0.000
Square	1	7.8	7.8	3.4	0.080
NCO : OH * NCO : OH	1	7.8	7.8	3.4	0.080
2-way interaction	1	17.1	17.1	7.5	0.013
NCO : OH * WA	1	17.1	17.1	7.5	0.013
Error	19	43 429.0	2 286.0		
Lack-of-fit	3	30 965.0	10.3	13.2	0.000
Pure error	16	12.5	0.8		
Total	23	498.0			

Model summary

S = 151186

R-sq = 91.3 % *R*-sq(pred.) = 87.2 % *R*-sq(adj.) = 89.4 %

Coefficients

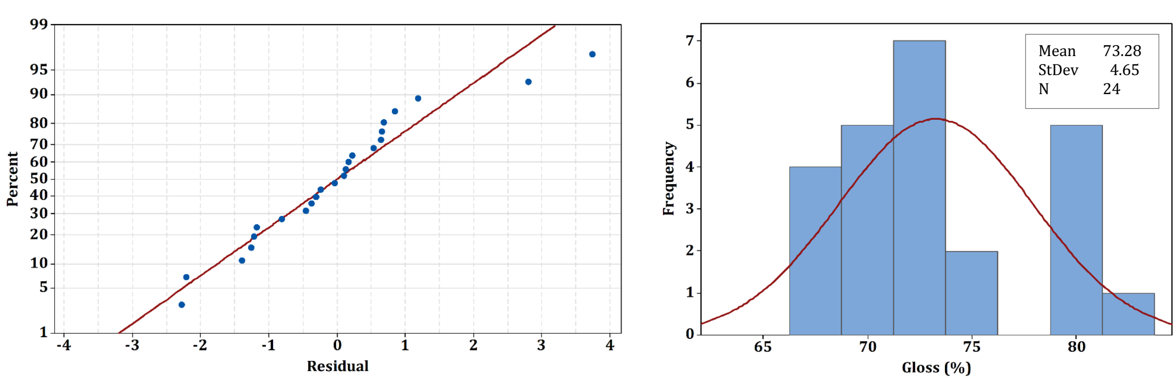
Term	Effect	Coef.	SE coef.	*T*-value	*p*-value	VIF
Constant		712.0	0.5	136.2	0.000	
NCO : OH	8.2	4.1	4.1	10.0	0.000	1.01
WA	5.6	2.8	0.3	8.9	0.000	1.01
NCO : OH * NCO : OH	2.7	1.3	0.7	1.8	0.080	1.01
NCO : OH * WA	2.2	1.1	0.4	2.7	0.013	1.03

Regression equation in uncoded units

Gloss = 227.2 – 252 NCO : OH – 183.9 WA + 93.4 NCO : OH * NCO : OH + 187.2 NCO : OH * WA

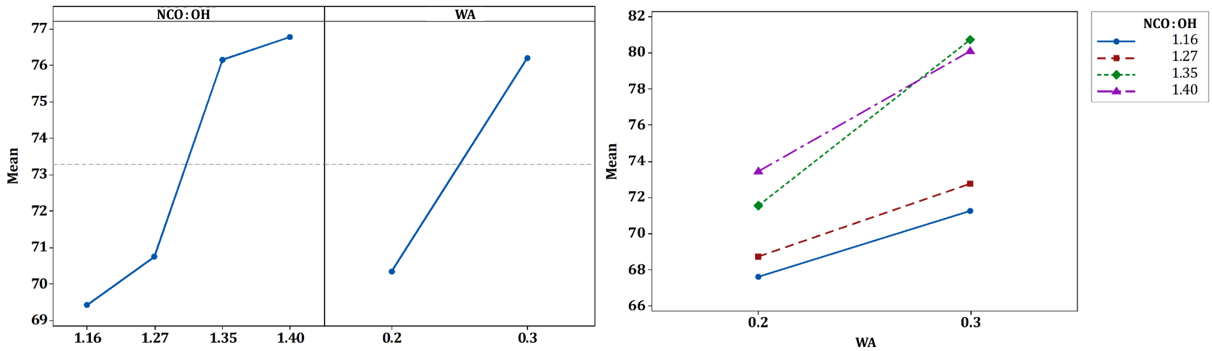
This is because resin R3 has smaller average particle size than resin R4, so even though the surface tension of resin R3 is slightly higher than that of resin R4, when it interacts with a surfactant, it helps to reduce the surface tension of ink up to the level which is sufficient to get a uniform layer of ink on LDPE surface. This condition highlights that the resin particle size also contributes to the gloss of ink.

The contour plot (Figure 12a) shows the lines for the same gloss percentage for different combinations of ink. Maximum gloss is observed at 0.3 % of the wetting agent and for the binder of 1.4 NCO : OH ratio. A surface plot displays the three-dimensional relationship in two dimensions, with the variables WA on the *x*-axis, NCO : OH on the *y*-axis, and the gloss response on the *z*-axis, represented by a smooth surface.



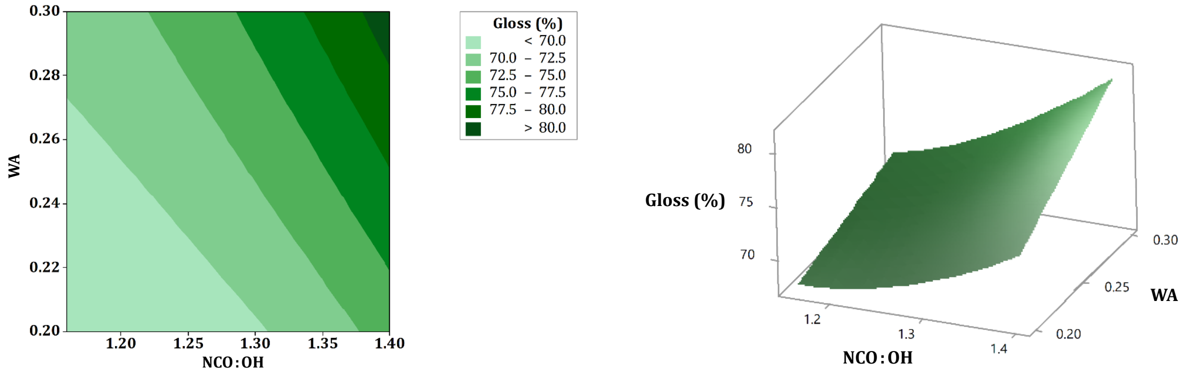
a) *b)*

Figure 10: Response of gloss: (a) normal probability plot, and (b) histogram



a) b)

Figure 11: Gloss values: (a) main effect plot, and (b) interaction plot for differnet NCO : OH ratios



a) b)

Figure 12: Gloss values vs WA content and NCO : OH ratios: (a) contour plot, and (b) surface plot

6.4 Validation trial

A validation trial was conducted for the optimized setting of ink ingredients (Table 14) for complete adhesion and maximum gloss. Results of validation trial are shown in Table 15.

Table 14: Ink formulation for validation trial

Ink ingredients	Amount (%)
Premixture	31.87
Binder	35.24
Wetting Agent	0.30
Polymer Emulsion	1.00
Water	31.59

Table 15: Characteristics of validation trial

Ink characteristic	Value
Gloss (%)	80.5
Adhesion (%)	100.0
Surface Tension (mN/m)	26.0
pH	8.7
Solids (%)	34.0
Viscosity (mPa·s)	220.0

6.5 Response optimizer

The response optimizer shown in Figure 13 uses the model equation to optimize the result. Response optimizer predicts that a maximum 81.3 % gloss of water-based ink on LDPE substrate will be observed when NCO : OH ratio of the PU resin is 1.4 and 0.3 % of WA is used in the formulation. Table 16 shows the values obtained from the response optimizer.

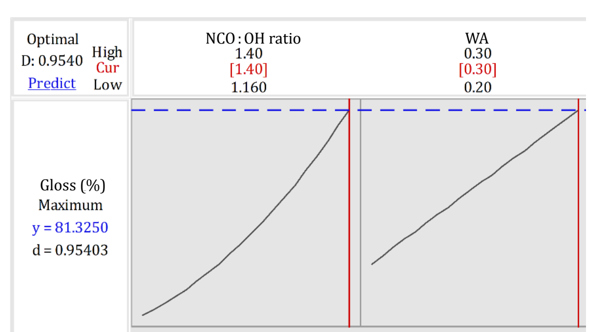


Figure 13: Response optimizer for gloss

Table 16: Response optimization for gloss of water-based ink
Response optimization: gloss

Parameters

Response	Goal	Lower	Target	Upper	Weight	Importance
Gloss	Maximum	67.1	82.0		1	1

Solution

Solution	NCO : OH ratio	WA	Gloss fit	Composite desirability
1	1.4	0.3	813 252	954 044

Multiple response prediction

Variable	Setting
NCO : OH ratio	1.4
WA	0.3

Response	Fit	SE Fit	95 % CI	95 % PI
Gloss	81.3	0.7	(79.8, 82.9)	(77.8, 84.8)

7. Conclusion

Mixture design model for all resins based on different NCO : OH ratio shows that interaction of resin with polymer emulsion and resin with a wetting agent are significant parameters for enhancing the adhesion of ink on the non-absorbent substrate. It was observed that adhesion values checked by the tape test are gradually increased from 1.16 to 1.4 NCO : OH ratio. Complete adhesion was observed for a binder which is based on 1.4 NCO : OH ratio.

For the lower NCO : OH ratio surface tension of the ink is higher due to higher number of hydroxyl value, which decreases the wetting of ink on LDPE film. Higher NCO : OH ratio reduces the surface tension of the ink, and increases the wetting of ink on LDPE film.

While formulating, the surface tension of ink and particle size distribution of resin interacts with the substrate wetting agent which significantly affects the gloss of the ink layer formed on the surface of the LDPE surface.

Regression model and response optimizer, optimize the complete adhesion and maximum gloss up to 80.5 % on LDPE substrate for 31.87 % dispersed pigment, 35.24 % of PU resin synthesized for 1.4 ratio of NCO : OH, 1 % of polymer emulsion, 0.3 % of surfactant and 31.59 % of deionized water.

Acknowledgment

Authors thank to M/s BYK India for providing additives and instrumentation facility. Thank to M/s Sudarshan Chemical Industries for providing pigment and instrumentation facility. Authors thank to M/s Kroslink polymer for providing polyurethane dispersions of specific properties. Corresponding author thanks to HoD, Mrs. Madhura Mahajan, and Principal of the college Dr. Y. P. Nerkar for the encouragement and extending the facilities for the completion of the research.

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