Egypt. J. Chem. **Vol. 67**, No. 2. pp. 215 - 229 (2024)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Preparation & Evaluation of white pigmented inkjet inks based on glycerol mono oleate - gallic acid as a dispersing agent for textile inkjet printing

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Abstract

The present study aims to prepare and evaluate white pigmented inks with home-made dispersing agent and investigate their physical and chemical characterization for inkjet printing on cotton fabric against white inks made by global dispersing agents, and focused on manufacturing of dispersing agent through the chemical reaction between glycerol mono oleate (GMO) and toluene diisocyanate (TDI). Subsequently, Gallic acid and modified succinic anhydride with PEG 600 which can be employed in water-based white pigmented inkjet inks. Fourier Transform Infrared Spectroscopy (FTIR) and Gel Permeation Chromatography (GPC) were employed to analyse the resultant dispersant and observe the advancement of the chemical reaction. In contrast with global available dispersants, an innovative constituent was developed to be used as an essential ingredient within white pigmented inkjet inks, featuring characteristics such as particle size distribution, dynamic surface tension, transmission electron microscopy (TEM), viscosity, and zeta potential. The investigation further encompassed the evaluation of the wash and crock fastness of the printed fabric utilizing the manufacturing inks. The obtained results indicate that the manufactured dispersing agent exhibited superior performance as compared to the industry benchmarks, particularly with regard to particle size distribution.

Keywords white pigmented inkjet ink, Dispersing agent, inkjet textile printing.

1. Introduction

Initially, dye-based inks such as acid dyes for silk, nylon, and wool, dispersion dyes for polyester, and reactive dyes for cotton and rayon were used in ink jet textile printing [1]. They all require complicated and not ecofriendly pre- and post-treatments to attain sufficient wash characteristics. These pre- and post-treatments partially negate the ease of customisation that digital printing was designed to provide. [1-5]. Conversely, pigment-based inks require only a simple dry heat post-treatment and are more adaptable in terms of fibre kinds [3]. The formulation of pigmented inks for ink jet digital textile printing comprises a dispersion of colour pigments along with the incorporation of a binder material such as latex, polymeric binder, or solution polymer to ensure the durability of the resultant images. [5-7]. Water serves as a vehicle for transporting additional constituents in the context of aqueous inkjet inks. Co-solvents enhance the efficacy of other constituents with respect to wetting, substrate adhesion, and jetting attributes by augmenting their solubility in water and promoting compatibility with it [7]. The utilisation of surfactants is widely implemented to ensure consistent moistening of nozzles and substrates, facilitate the jetting process, and effectively stabilize pivotal constituents, namely binder and pigment particles, to avert coagulation. Humectants demonstrate the ability to impede the process of dehydration without resulting in the printing. In order to mitigate excessive foaming, it is recommended to utilise an antifoam agent. A substance with viscosity-controlling properties is

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Received date 24 May 2023; revised date 06 August 2023; accepted date 08 August 2023
DOI: 10.21608/ejchem.2023.213067.8014

utilized for the purpose of managing damping and droplet formation, while a biocide is employed in order to prevent bacterial growth [8-14]. There is a need for improved pigment selection, especially for a stable aqueous ink for inkjet inks. In particular, there is a need for white pigments that can be sufficiently stabilised in inkjet compatible formulations so that the resultant ink can be effectively jetted, even after being stored for some period of time with a minimum of mixing prior to the jetting process. [9-13]. In addition, the ability to use an ink containing a white pigment to complement other inks in an ink set can lead to improved images, especially when lighter tones and/or higher degrees of coverage or opacity are needed. The need for a white ink is particularly important for printing on non-white substrates, especially non-white textiles. There is a need for an ink formulation containing a white pigment for use in inkjet systems that provides the needed effects of a white ink, especially for printing images on coloured textiles. There is still need for an aqueous system that includes all these benefits. [10,14].

Dispersing agents are an addition used in coating materials to make it easier for the solid components to mix with the liquid phase during manufacturing, improve stability, and improve storage. A homogenous distribution of materials in a liquid medium is called dispersion. The adhesion strengths of the tiniest solid particles must be overcome during the dispersion process. [5,11,12] Wetting, separation, and stability are the three steps that make up the dispersion process. Dispersing agents are typically complex polymers with a pigment affinic group that adheres to the surface of the pigment particle (OH, COOH, NH2, NR2, aryl, nitrile, amide, etc.) [11,13] and a solvent affinic chain (tail) that extends in solution to provide steric stabilization against re-agglomeration. [14-16] Polyurethanes (PUs) have been widely employed due to their superior physical qualities and chemical structural adaptability. [17-22]. Because typical polyurethane is insoluble in aqueous conditions, ionic and/or non-ionic hydrophilic segments should be introduced into its backbone structure to make it water dispersible. [23-25]. To make inkjet ink, pigment particles must be dispersed in liquid; the dispersion process required total wetting of the particles. The stability of the pigment dispersion is critical, particularly for inkjet printing inks. [26-28]. The use of specialised additives to reduce surface tension and enhance pigment wetting is required to maintain the stability of pigments in non-aqueous mediums. Pigment particle sizes should be fewer than 300 nanometres to prevent clogging of the important and costly print head. [27]. The pigment particles can be broken down and kept from recombining into large-sized particles by introducing dispersion agents to the ink manufacturing process. [29-32]. According to repulsive forces between the particles in suspension are produced by the adsorption of dispersing agent molecules from solution onto the pigment particle surface. These forces can be electrostatic repulsion or steric prevention of coagulation. Dispersing agents are an addition that is used in coating materials to increase stability, improve storage, and make it simpler for the solid components to mix with the liquid phase during manufacture. Dispersion is the uniform distribution of elements in a liquid media. The dispersion process requires overcoming the adhesion strengths between the smallest solid particles. [11,12]. The dispersion process consists of three steps: wetting, separation, and stability. The pigment-wetting method includes displacing air from the surface of the pigment with the carrier (resin) and wetting the particles. [33-35].

The current study's goal is to produce a prepolymer act as dispersing agents for titanium dioxide water-based inkjet inks. At a cheap cost, this dispersant provides good performance, stability, and have a low environmental impact. Glycerol mono oleate (GMO) was combined with toluene di isocyanate (TDI) to produce GMO-TDI prepolymer, which was then combined with Gallic acid and modified succinic anhydride -PEG 600 to produce a dispersing agent for water-based titanium dioxide inkjet inks.

2. Experimental

2.1. Materials

The present study incorporates the utilization of several commercial chemical compounds for various purposes in the formulation of a product. Specifically, Huntsman-USA's titanium dioxide is employed as a colorant, while Troy-USA's Acticide K14 is utilized as a preservative. Additionally, BYK-Germany's BYK 019 is added as a defoamer, BYK 348 as surfactant and Sigma-Aldrich's N-Methyl Pyrrolidone is employed as a solvent. Further, Sigma-Aldrich's propylene glycol is incorporated as a humectant. Covestro-Germany's TDI, Alpha chemicals-India's succinic anhydride and PEG 600, Petrochem-Egypt's ethyl acetate are also utilized as key constituents. Finally, commercial

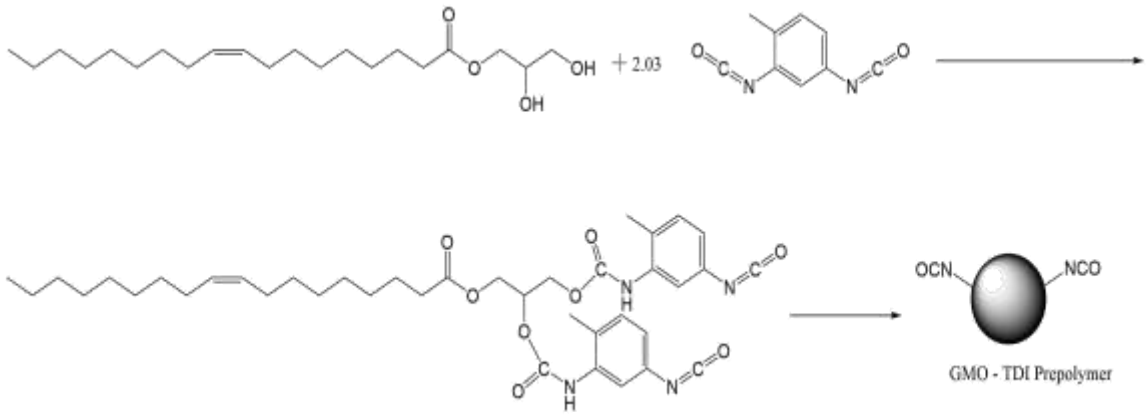
dispersing agents like Dispersing 2, 3 (Evonik-Germany), Dispersing 1, 4, 5 (BYK-Germany), Dispersing 6, 7 (Basf-USA), and Dispersing 8 (Esna Chemicals-Egypt) are added for dispersing purposes.

2.2. Methods

2.2.1. Reaction of glycerol mono oleate and toluene diisocyanate (GMO-TDI).

At a temperature range of 55 to 60 degrees Celsius, an amount of 2.03 moles of toluene diisocyanate (TDI) dissolved in ethyl acetate was subjected to thermal treatment. Subsequently, one mole of glycerol mono oleate (GMO) was systematically introduced while carefully monitoring the temperature to ensure that it does not exceed 60°C.

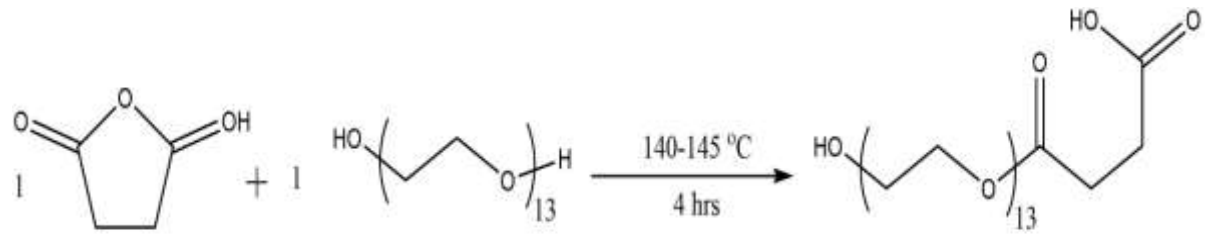
The Non-Volatile Matter (NVM) underwent a 40% modification to yield an intermediate of low viscosity subsequent to the completion of the reaction. Monitoring the modification was achieved by employing Fourier Transform Infrared Spectroscopy (FTIR) until the entire OH band was exhausted. The chemical composition of Prepolymer is represented in scheme 1.



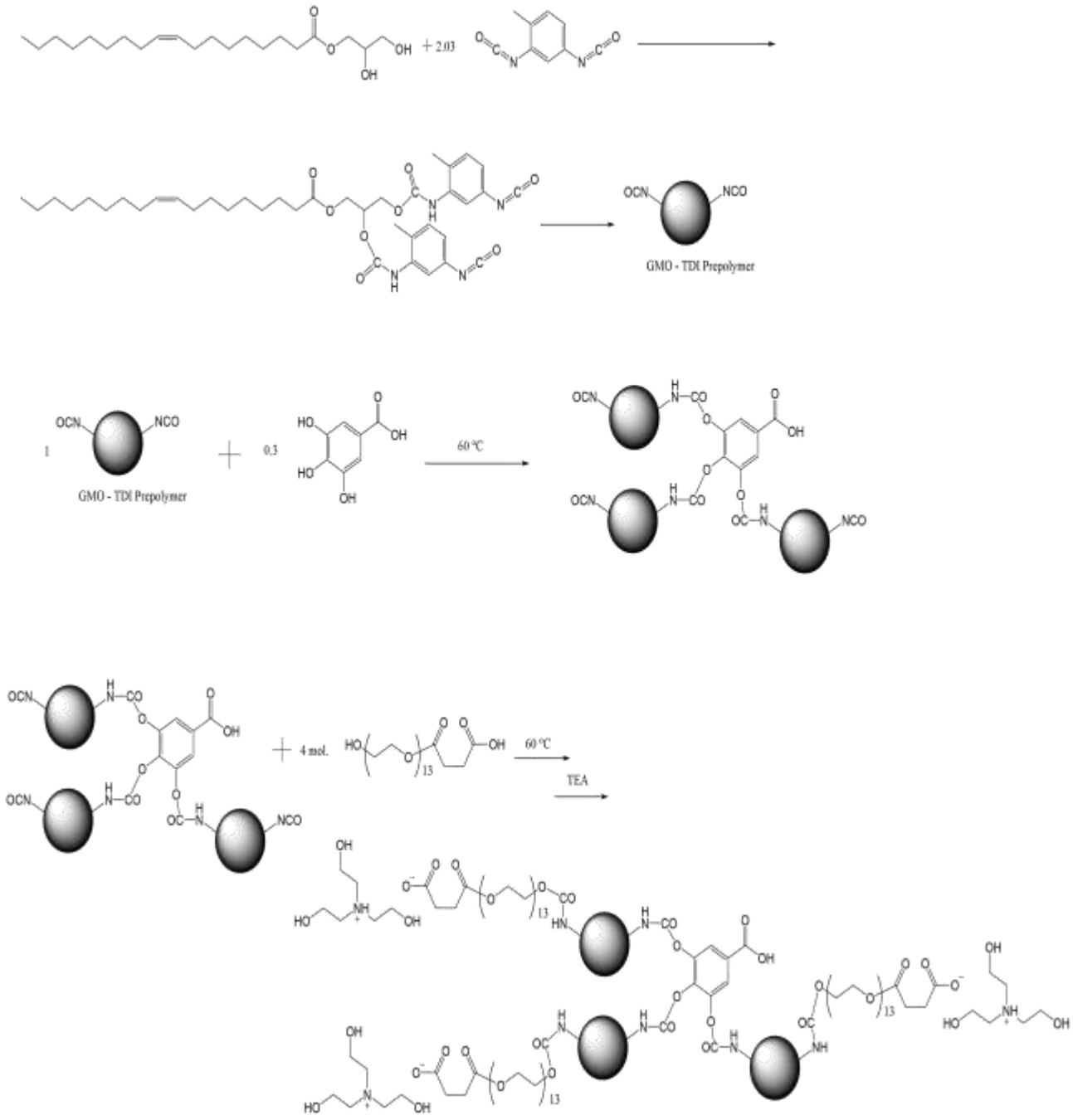
Scheme 1 Chemical Composition of GMO-TDI Prepolymer

2.2.2. *Reaction of succinic anhydride with* polyethylene glycol 600.

Based on the reaction mass analysis, a conical flask that contained a combination of 1.1 moles of PEG 600 and 1 mole of succinic anhydride underwent heating at temperatures ranging between 140 and 145°C. The reaction was subsequently terminated after a duration of 7 hours once a complete depletion of the acid anhydride was verified through FTIR measurement. The mentioned product features a succinate carboxylic acid present at the polyethylene glycol (PEG) terminal end. Scheme 2 illustrates the chemical composition of succinic anhydride-modified polyethylene glycol 600.



Scheme 2 Chemical composition of succinic anhydride modified PEG 600.



Scheme 3 Preparation of dispersing agent ES using the above prepared prepolymer.

2.2.3. Synthesis of Dispersing agent ES (D8)

A solution containing 0.3 moles of Gallic acid was subjected to dilution using N-Methyl-2-Pyrrolidone in a ratio of 1:10. The resulting solution was gradually introduced to 1 mole of a prepolymer solution in ethyl acetate heated to 60°C. The conducted reaction was sustained at the aforementioned temperature until the complete exhaustion of all hydroxyl (OH) groups, as evidenced by Fourier Transform Infrared Spectroscopy (FTIR) analysis in figure 3. Scheme 3 illustrates the chemical composition of dispersing agent D8.

2.2.4. The development of an inkjet ink formulation utilizing previously prepared dispersing agent.

The selection of deionized water, titanium dioxide pigment, solvents, humectants, defoamer, and biocide was based on ink formulations for the ink configuration process [11].

The mixed solution compounded herein involves combining 5gm of N-Methyl-2-pyrrolidone (NMP) with varying amounts of the dispersing agent in differing concentrations: 4.5gm (30%), 6gm (40%), 7.5gm (50%),

and 9gm (60%). Subsequently, incorporate 15 grams of titanium dioxide, 0.9 grams of BYK 019, and 0.1 grams of Acticide MBS. Subsequently, the solution ought to be homogenized by the gradual inclusion of up to 100 millilitres of deionized water. Once the aforementioned step has been accomplished, 30 grams of zirconia beads with a diameter of 0.3 millimetres should be added in a closed cup with a capacity of 100 millilitres. Following this, the mixture ought to be subjected to shaking using a coating quick mixer with the model designation BGD 760 for a duration of two hours.

In this experimental study, eight distinct dispersion agents were utilized, each possessing unique concentration ratios, resulting in a total of 36 samples. Subsequently, as delineated in Table 1, diverse compositions of inkjet ink specialized for textile application were developed for the purpose of this research.

Whilst keeping all other constituent's constant, the concentration of the dispersing agent was varied from 30% to 60%.

Table 1 Formulation of the Prepared inkjet inks.

Mill base				
Component/Dose	**30%**	**40%**	**50%**	**60%**
White Pigment TiO_2	**15**	**15**	**15**	**15**
Dispersing agents (1,2,3,4,5,6,7,8)	**4.5**	**6**	**7.5**	**9**
BYK 019	**0.9**	**0.9**	**0.9**	**0.9**
NMP	**5**	**5**	**5**	**5**
K14	**0.1**	**0.1**	**0.1**	**0.1**
Finished ink				
Mill base	**25**	**25**	**25**	**25**
Propylene Glycol	**20**	**20**	**20**	**20**
BYK 348	**0.2**	**0.2**	**0.2**	**0.2**
DSM Binder	**18**	**18**	**18**	**18**
Water	**36.8**	**36.8**	**36.8**	**36.8**

2.2.5. Characterization

2.2.5.1. Gel Permeation Chromatography (GPC):

Agilent model 1515 pump system equipped with 1260 infinity refractive index detector and using THF as eluent. Operating with a flow rate of 1.00 ml/min at 35℃. Column PL-gel 3 lm Mixed E 300 7.5 mm covering a molecular weight range of 600–400,000 mg/g was used and was calibrated using polystyrene standards.

2.2.5.2. Bruker Fourier Transform Infrared Spectroscopy (FTIR) analyser

The ALPHA-Platinum Fourier Transform Infrared (FT-IR) Spectrometer, equipped with the Attenuated Total Reflectance (ATR) Platinum-Diamond sampling module, is capable of measuring infrared spectra within the wavelength range of 400 to 4000 cm^{-1}.

2.2.5.3. Viscosity DV-E Viscometer

The measurement of the apparent viscosity of the ink was conducted using a Brookfield DV-E viscometer, which features coaxial cylinder spindles, sample cups, and a water circulating jacket. The ink that had been prepared was introduced into the cylindrical cell of the viscometer and subjected to testing under controlled conditions. The temperature remained constant at 25 °C, while the shearing speed varied within the range of 0-60 S^{-1}.

2.2.5.4. Dynamic surface tension (DST)

The evaluation of the inks was conducted employing the SITA pro line T15 bubble pressure tensiometer. The measuring instrument exhibits a broad spectrum of bubble lifetimes, spanning between 15 milliseconds and 20 seconds. This functionality caters to a diverse concentration range, encompassing quantities ranging from several grams to a few micrograms of surfactant. The measurement of Dynamic Surface Tension (DST) conforms to the

standards stipulated by the American Society for Testing and Materials, specifically the ASTM D 3825-90 protocol.

2.2.5.5. Particle Size Distribution (PSD)

The analysis of particle size distribution was performed based on the guidelines outlined in ASTM D4464 – 00, utilizing The Mastersizer 3000's measurement size range spanning from 10 nanometres to 3.5 millimetres. To obtain the average particle size, each sample was measured thrice. The dispersion of the samples was accomplished by employing the supplemental Hydro EV apparatus.

2.2.5.6. Transmission electron microscopy (TEM)

Alternatively denote the equipment of a transmission electron microscope (TEM), is a microscopy methodology that employs a beam of electrons transmitted through a sample to generate an image.

2.2.5.7. Zeta potential measurement

The Horiba SZ-100-V2, A singular apparatus evaluates the three components including particle size, zeta potential, and molecular weight.

The measurement of zeta potential was conducted via the utilization of Laser Doppler electrophoresis, with a measurement range spanning from negative five hundred to positive five hundred millivolts.

3. Results and discussion

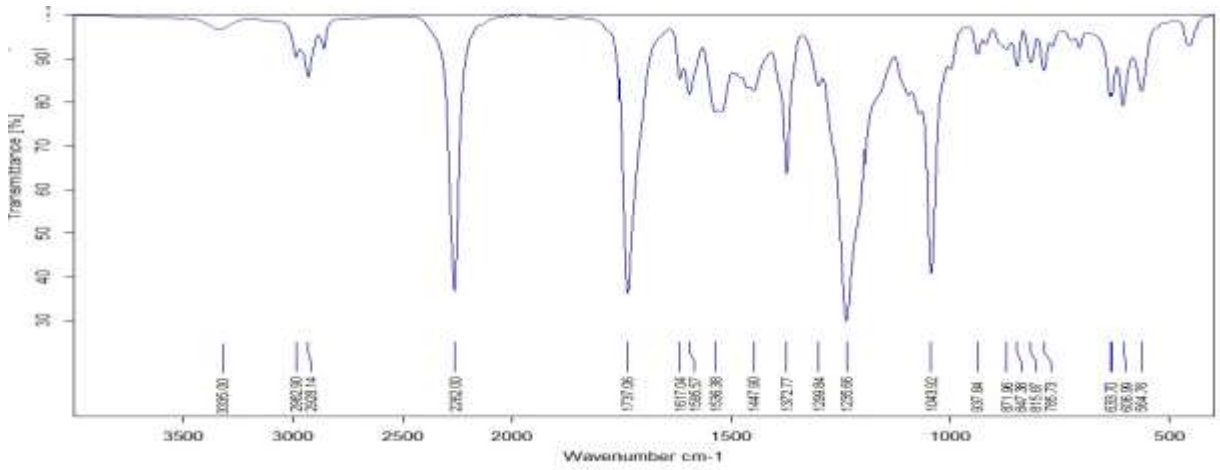
3.1. Characterization of the created prepolymers

3.1.1. FTIR

3.1.1.1. FTIR of prepared prepolymer synthesis GMO-TDI

It was noticed that the area of the peak for isocyanate NCO at (2261 cm-1) would decrease by 50%; however, this was not observed. This was due to the fact that during the addition stage, a large portion of the isocyanate had already reacted, which is necessary to avoid the formation of gel-like substances and unwanted by-products. Figure 1 illustrates the significant response, which was indicated by the presence of the hydroxyl OH peak within the range of 3450-3550 cm-1. After depletion of the hydroxyl peak, a noticeable surge in the peak observed at (3300 cm-1), which reflects the N-H stretching of the recently formed urethane bond, is evident. it was observed that the C=O stretching of the newly synthesized urethane is indicated at a frequency of 1707 cm^{-1}.

Figure 1 FTIR OF the prepared Prepolymer based on GMO-TDI



3.1.1.2. FTIR of prepared succinic anhydride modified PEG 600

As the reaction progresses, the anhydride peak located at a wavenumber of 1847 cm-1 The C-O stretching of ether is responsible for the peak observed at 1092 cm-1and the C=O peak associated with the acid group at 1776 cm-1 undergo a reduction in their intensity. Conversely, a new peak corresponding to the formation of ester linkage emerges at 1731 cm-1. The absorption peak observed at 3481 cm-1 be attributed to the hydroxyl group of polyethylene glycol (PEG) and the carboxylic group of succinic. The C-H stretching manifests as a peak at 2865 cm-1, as illustrated in Figure 2.

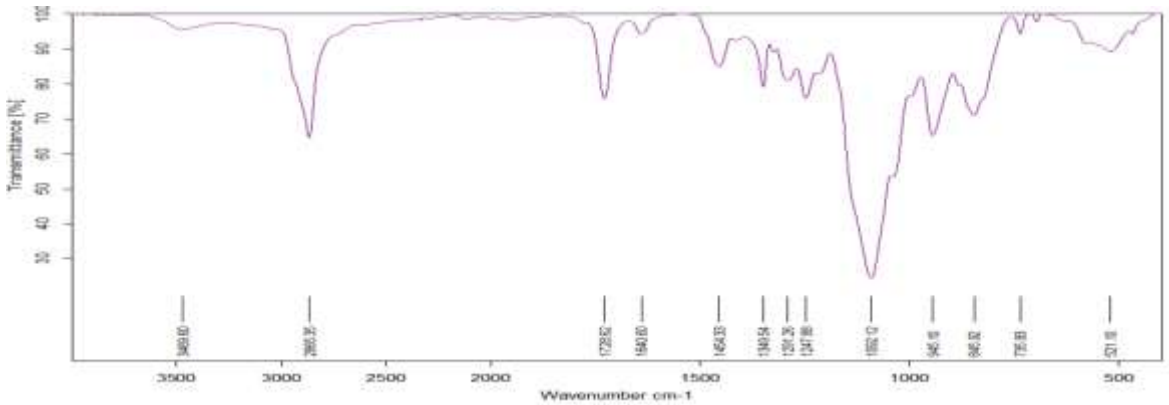


Figure 2 FTIR OF succinic anhydride modified PEG 600.

3.1.1.3. FTIR of prepared dispersing agent DA8

The observed peak at 3470 cm-1 is a result of the N-H urethane and OH ether PEG, whereas the peaks indicating C-H stretching appear at 2872 cm^{-1}. Furthermore, as illustrated in the figure 3. The C-O stretching of the ether is responsible for the peak observed at 1092 cm-1, while the C=O of the (N-H-C=O) group is attributed to the peak observed at 1736 cm^{-1}.

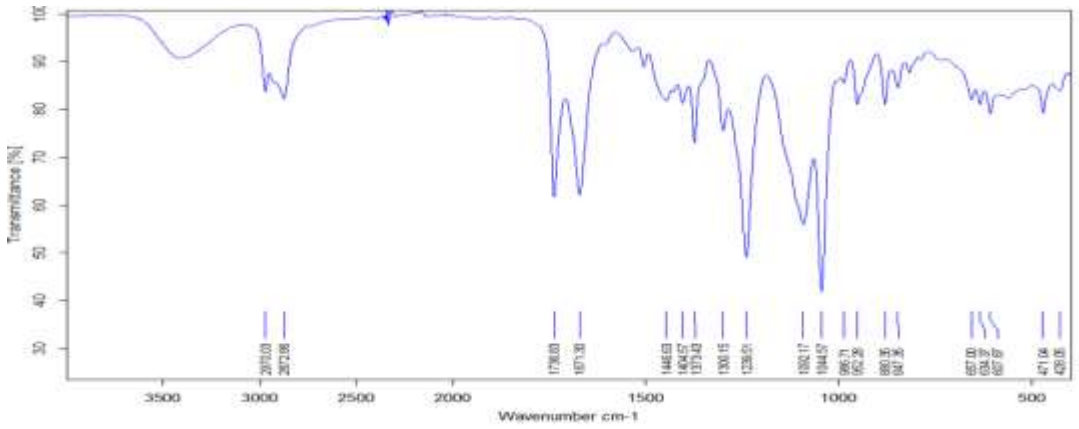


Figure 3 FTIR OF dispersant ES (D8).

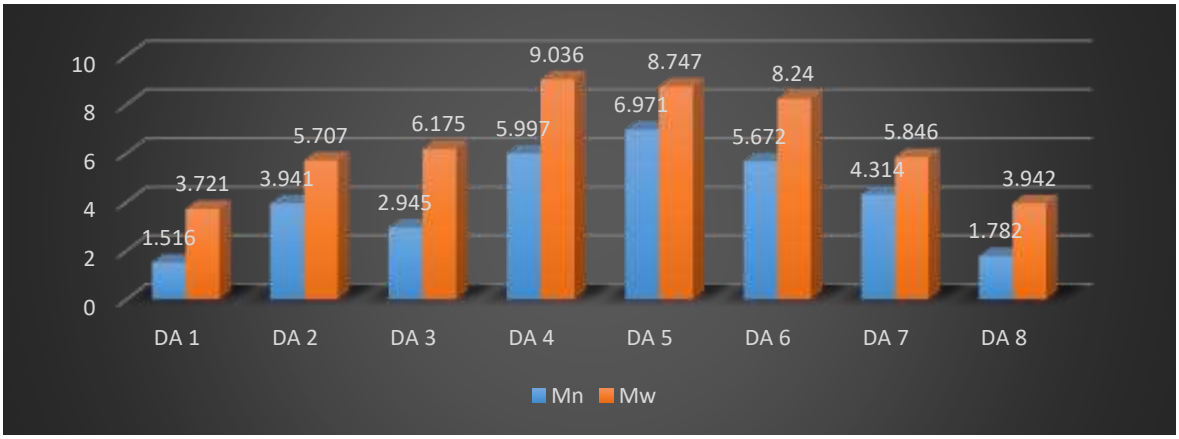


Figure 4 GPC values of the used dispersing agents.

3.2. GPC

The properties of a polymer are greatly influenced by its molecular weight. It was imperative to confirm the molecular weights of the dispersing agents fabricated in-house (DA8) and those obtained from the market. This was carried out by assessing their molecular weights through GPC approach, as showcased in figure 4 and table 2.

Table 2 GPC results of used dispersing agents.

Sample Name	Sample Code	Mn	Mw	PDI
White 15% W 190	**DA 1**	**1.516**	**3.721**	**2.454485**
White 15% W 755	**DA 2**	**3.941**	**5.707**	**1.44811**
White 15% W 757	**DA 3**	**2.945**	**6.175**	**2.096774**
White 15% W 9171	**DA 4**	**5.997**	**9.036**	**1.506753**
White 15% W 9151	**DA 5**	**6.971**	**8.747**	**1.25477**
White 15% W 4585	**DA 6**	**5.672**	**8.24**	**1.45275**
White 15% W 4560	**DA 7**	**4.314**	**5.846**	**1.355123**
White 15% W ES	**DA 8**	**1.782**	**3.942**	**2.212121**

3.3 Physical characteristics of the prepared inkjet inks

3.3.1. Viscosity measurements:

Inkjet printing relies significantly on the ink viscosity, since high viscosity inks cannot be ejected through the printhead nozzles, and low viscosity ones may disintegrate during the ejection process, resulting in erratic or scattered droplets that can alter the printed design.

The printing process is rendered intricate. An effective dispersing agent operates as a lubricant that lowers interactions and frictions between particles, leading to decreased viscosities, indicative of a well-dispersed system. In contrast, an inadequate dispersant exhibits a reduced level of coverage on the particles' surfaces, thereby promoting inter-particle interaction, which can result in elevated viscosity levels based on the number of exposed surfaces present [36-38].

The present investigation revealed that Dispersant DA8 exhibits superior viscosity properties relative to Dispersants DA1, DA2, DA3, and DA7. This is attributed to the prominent presence of aliphatic chain side groups rich in softening and hydrogen-bond hindering properties, which are characteristic of succinic anhydride modified polyethylene glycol chains. On the other hand, Dispersants DA4, DA5, and DA6 exhibit viscosity levels that surpass those of their counterparts in a manner consistent with their respective molecular weights and particle sizes.

The viscosity of all specimens was assessed at a temperature of 25°C both prior to and following the accelerated stability trial, and the findings concurred with those of the particle size analysis examination. Table 3 and Figure 5 present the entirety of the data in cP units.

Table 3 Viscosity results of the prepared inkjet inks.

Sample Name	Sample Code	30% B. S	30% A. S	40% B. S	40% A. S	50% B. S	50% A. S	60% B. S	60% A. S
White 15% W 190	**DA 1**	**3.2**	**3.8**	**3.3**	**3.5**	**2.8**	**3**	**2.7**	**2.9**
White 15% W 755	**DA 2**	**3.7**	**4**	**4.2**	**4.5**	**4.2**	**4.5**	**3.7**	**4**
White 15% W 757	**DA 3**	**3.8**	**3.9**	**3.8**	**4**	**4.5**	**4.4**	**3.8**	**4.3**
White 15% W 9171	**DA 4**	**9**	**15**	**8.5**	**11**	**7.2**	**9**	**7**	**14**
White 15% W 9151	**DA 5**	**8**	**12**	**7**	**7.8**	**7.8**	**10.8**	**8.9**	**13**
White 15% W 4585	**DA 6**	**4.9**	**5.5**	**4.9**	**5.5**	**3.5**	**3.8**	**3.8**	**4**
White 15% W 4560	**DA 7**	**4.1**	**5.3**	**4**	**4**	**4.4**	**4.2**	**3.6**	**3.8**
White 15% W ES	**DA 8**	**3.6**	**3.9**	**3.8**	**4.1**	**2.9**	**3.1**	**2.4**	**2.6**

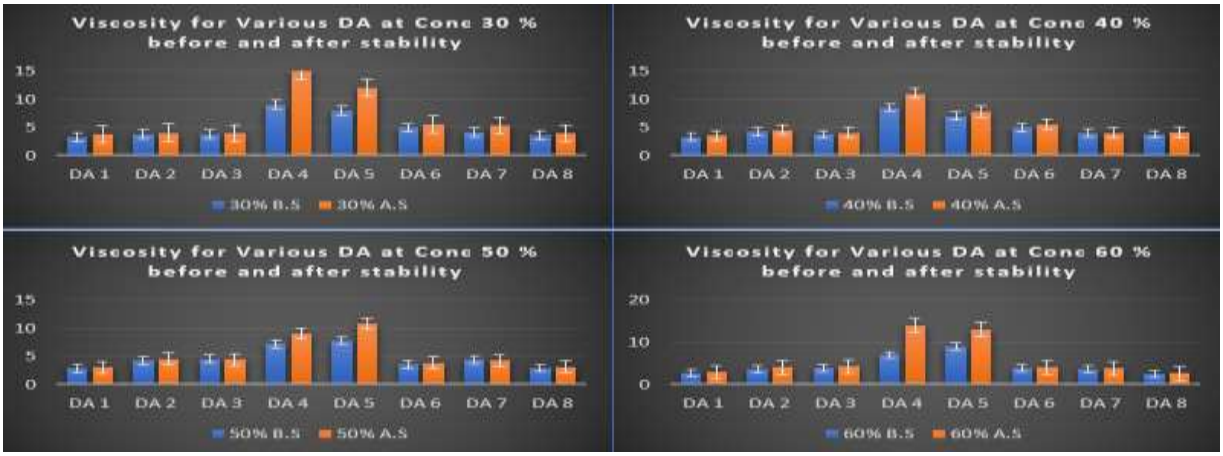


Figure 5 Viscosity for various dispersing agents at different concentrations before and after stability.

3.3.2. Dynamic Surface Tension measurement:

Surface tension measurements were conducted both prior to and after the accelerated stability assessment with all samples being evaluated at a temperature of 25°C. Further details and an overview of the findings are presented in Table 4 and Figure 6.

Table 4 Dynamic surface tension results of the prepared inkjet inks.

Sample Name	Sample Code	30% B. S	30% A. S	40% B. S	40% A. S	50% B. S	50% A. S	60% B. S	60% A. S
White 15% W 190	**DA 1**	**46**	**45.2**	**44.6**	**47**	**45.2**	**44**	**46.8**	**46**
White 15% W 755	**DA 2**	**43.3**	**45**	**43.3**	**46.5**	**44.2**	**43.5**	**46.2**	**45**
White 15% W 757	**DA 3**	**38.1**	**40**	**37.7**	**40**	**38.6**	**37**	**38.7**	**39.7**
White 15% W 9171	**DA 4**	**46**	**45.7**	**45.4**	**47.8**	**45.7**	**45**	**47.3**	**46**
White 15% W 9151	**DA 5**	**47.8**	**48**	**47.2**	**49**	**47.7**	**48**	**48.3**	**51**
White 15% W 4585	**DA 6**	**47**	**46.5**	**46.5**	**47**	**46.5**	**46.5**	**47**	**48**
White 15% W 4560	**DA 7**	**42**	**41.7**	**41.7**	**43**	**41.7**	**43**	**42.9**	**43**
White 15% W ES	**DA 8**	**40**	**39.4**	**39.7**	**41.5**	**39.4**	**40**	**40.5**	**42**

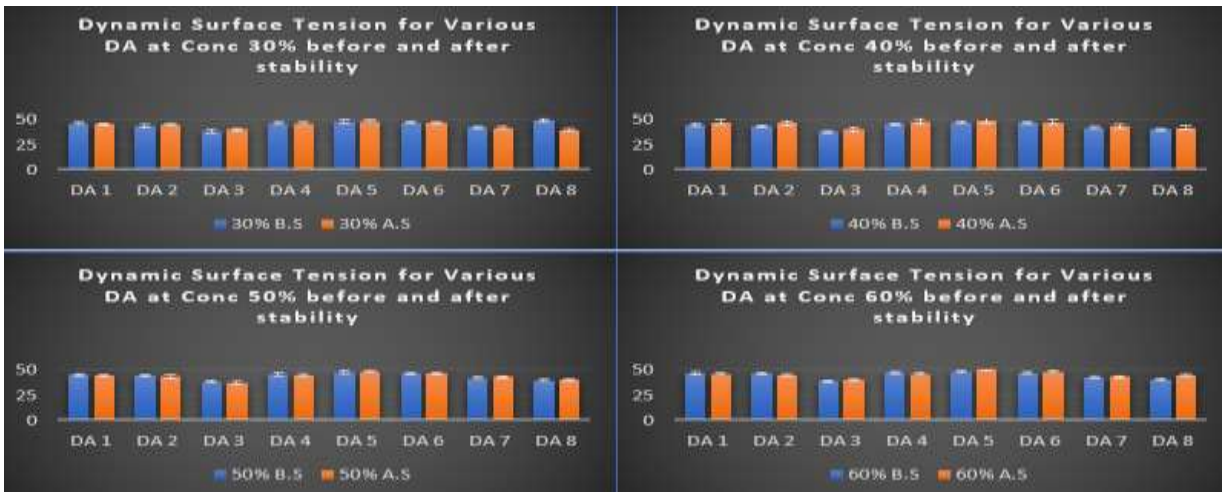


Figure 1 Dynamic surface tension for various dispersing agents at different concentrations before and after stability.

A comparison of the results obtained prior to and following the stability test provides insight into the dispersant activity and actual affinity towards the surface of the pigment [39-43]. The assessment of the interfacial interaction between dispersants and pigments is facilitated by the utilization of surface tension measurement as a valuable tool. Following the stability test, it has been observed that dispersants demonstrating favourable wettability and particle size characteristics tend to exhibit a more distinct decline in surface tension. This phenomenon can be observed in the case of Dispersant DA1 standard (44-47) dyne/cm, as well as the dispersants denoted by the labels, DA2 (43-47) dyne/cm, DA3 (37-40) dyne/cm, DA4 (45-548) dyne/cm, DA5 (47-51), DA6 (46-48) dyne/cm., DA7 (41-43) dyne/cm and DA8 (39.5-42) dyne/cm. This is due to the fact that in all samples, the majority of the dispersant was adsorbed on the titanium dioxide pigment surface.

This study indicates that each sample was efficacious in reducing the surface tension of a water-based ink containing titanium dioxide pigment, while simultaneously ensuring that the dynamic surface tension remained at an acceptable level [43].

Poor dispersants like DA4, DA5 and DA6 on the other hand, already exhibited poor adsorption on the TiO_2 surface. These were mainly responsible for the fresh samples' reduced surface tension. Although the dispersant was already present in the bulk from the beginning and this is matched to the results of the particle size distribution, surface tension remains quite close to the initial results even after stabilization.

3.3.3. Zeta Potential Measurements

The surrounding environment of a particle and the composition of ink solids play a crucial role in determining the Zeta potential. ZP analysis incorporates the use of electrophoretic light scattering (ELS) and electroacoustic evaluation techniques. In comparison to alternative methods, ELS provides superior precision and more reliable results. Nanoparticles possess a small scale, extensive surface area, and unrestrained energy, which may result in the bunching together of coloring agents. [44] This parameter reflects the level of repulsion exhibited by the charged particles present in the dispersion towards one another. The phenomenon of electrostatic repulsion leads to the inhibition of particle aggregation by highly charged particles that possess a significant surface charge density, typically referred to as high ZP. When the value of the Zeta Potential (ZP) is low, the dominant interaction between particles becomes attraction instead of repulsion, resulting in an increased likelihood of coagulation within the mixture. It is customary to draw the border between stable and unstable suspensions at either +30 or -30 mV. In general, stable particles are those with zeta potentials more positive than +30 mV or more negative than -30 Mv [44,45,53]. Even though they are scattered, particles with a density larger than the dispersant will eventually settle and create a densely packed bed. The outcomes of testing ink stability with different dispersing agents are listed in table 5 and figure 7.

Table 5 Zeta Potential values of some prepared inkjet inks.

Sample Name		**DA 1**	**DA 3**	**DA 5**	**DA 7**	**DA 8**
Temperature of the Holder	**°C**	**24.8**	**24.9**	**24.8**	**24.8**	**25**
Dispersion Medium Viscosity	**mPa·s**	**0.899**	**0.897**	**0.899**	**0.898**	**0.896**
Conductivity	**mS/cm**	**0.212**	**0.211**	**0.211**	**0.211**	**0.211**
Electrode Voltage	**V**	**3.3**	**3.3**	**3.4**	**3.3**	**3.4**
		Calculation Results				
Zeta Potential						
Zeta Potential (Mean)	**mV**	**-76.5**	**-87.3**	**-17.7**	**-75.9**	**-73.4**
Electrophoretic Mobility Mean	**cm2/Vs**	**-0.00059**	**-0.00068**	**-0.00014**	**-0.00052**	**-0.00059**

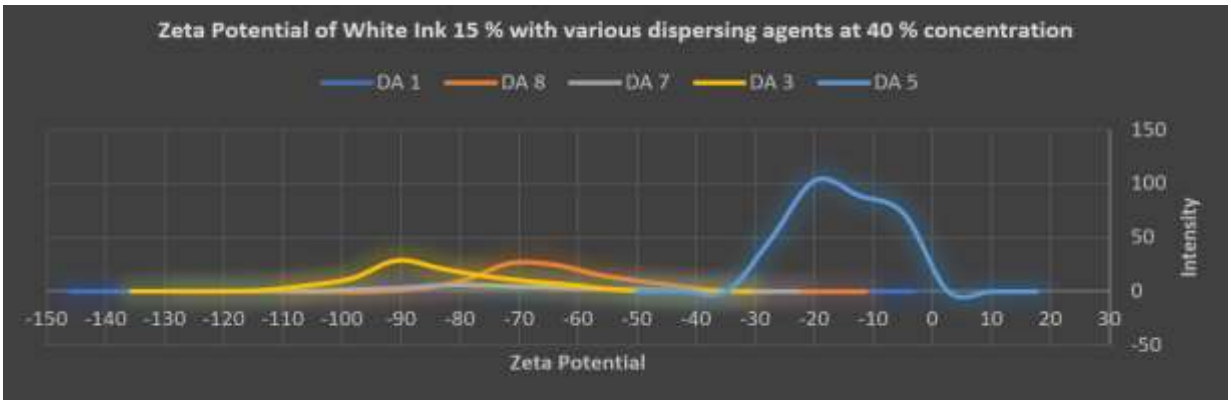


Figure 2 Zeta potential of TiO2 inkjet ink 15% with various dispersing agents

The ZP results for dispersants DA8 was -73.4, indicating stability and demonstrating greater effectiveness in achieving optimal viscosity and particle size compared to dispersants DA1 and DA3. Dispersant DA5 on the other hand, showed unstable ZP (-17) as well as poor particle size distribution results.

3.3.4. Particle Size Distribution Measurements:

In order to maintain stability and reduce particle size, the dispersing agent must exhibit a high level of compatibility with both the media in which it is dissolved and the pigment surface [38,46,47]. This is particularly important in comparison to the norms observed within the industry as outlined in this study. Additionally, successful dispersal requires a strong bonding between the dispersant and the pigment surface, which is facilitated by strong wettability, especially in water-based systems. The findings of the particle size analysis of the generated inks prior and subsequent to the accelerated stability test are exhibited in Table 6 and Figure 8

.

Table 6 Particle Size results of the prepared inkjet inks.

Sample Name	Sample Code	30% B. S	30% A. S	40% B. S	40% A. S	50% B. S	50% A. S	60% B. S	60% A. S
White 15% W 190	**DA 1**	**0.521**	**0.612**	**0.475**	**0.563**	**0.51**	**0.628**	**0.484**	**0.526**
White 15% W 755	**DA 2**	**0.526**	**0.654**	**0.468**	**0.468**	**0.462**	**0.528**	**0.522**	**0.687**
White 15% W 757	**DA 3**	**0.614**	**0.628**	**0.527**	**0.564**	**0.492**	**0.528**	**0.496**	**0.569**
White 15% W 9171	**DA 4**	**246**	**420**	**158**	**305**	**264**	**425**	**230**	**426**
White 15% W 9151	**DA 5**	**1.39**	**1.54**	**1.4**	**2.31**	**1.11**	**3.87**	**81.2**	**115**
White 15% W 4585	**DA 6**	**48**	**56**	**39.9**	**54**	**0.575**	**0.575**	**0.733**	**2.6**
White 15% W 4560	**DA 7**	**0.502**	**0.568**	**0.503**	**0.564**	**0.613**	**0.756**	**0.622**	**0.877**
White 15% W ES	**DA 8**	**0.468**	**0.498**	**0.425**	**0.461**	**0.511**	**0.578**	**0.549**	**0.518**

The particle size of the inks containing DA4, DA5 and DA6 dispersants was found to be the greatest among other dispersants (158,1.4,39.9 µm) respectively. This can be attributed to their large molecular weight and the low adhesiveness of their anchor group to the surface of the titanium dioxide pigment [46-47]. The findings regarding the distribution of particle sizes were consistent with the results obtained from the measurements of viscosity and GPC.

The particle size distribution achieved by dispersant DA8 (0.425 µm) was comparable to that obtained by the standard dispersant DA1 (0.475 µm). Furthermore, due to the surplus polyether chains comprising carboxylic groups that contribute to electrostatic stabilization, as well as lengthy alkyl chains that result in steric stabilization of the dispersant in its entirety, the superior performance of DA8 as a dispersant was noted in comparison to the conventional option [47-52].

All the findings were verified through TEM outcomes of the dispersing agents, seen in Figure 9.

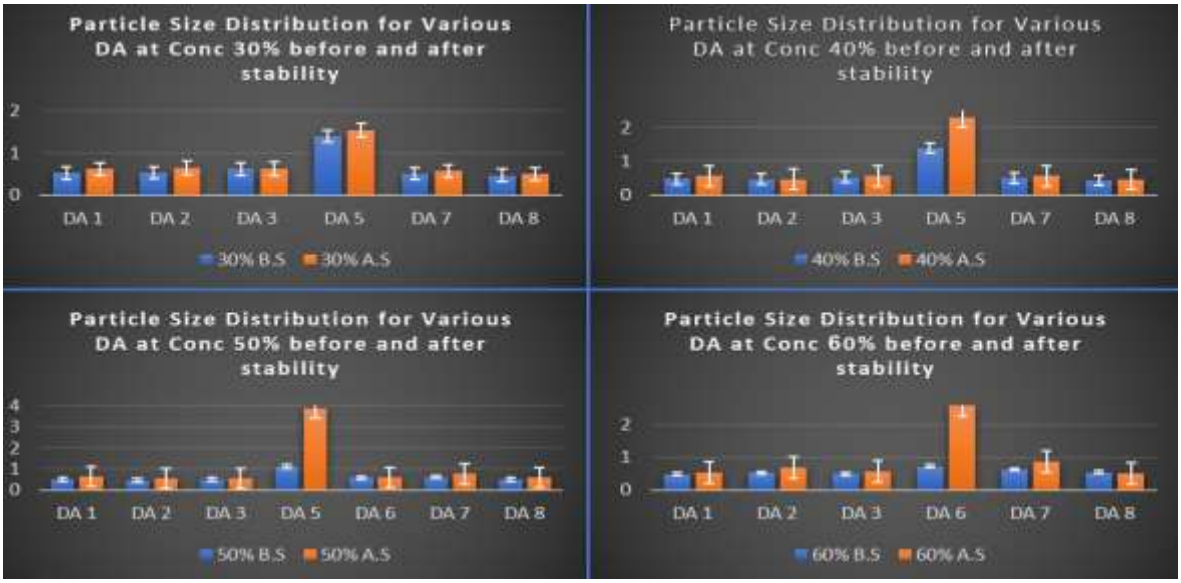


Figure 3 Particle size distribution for various dispersing agents at different concentrations before and after stability.

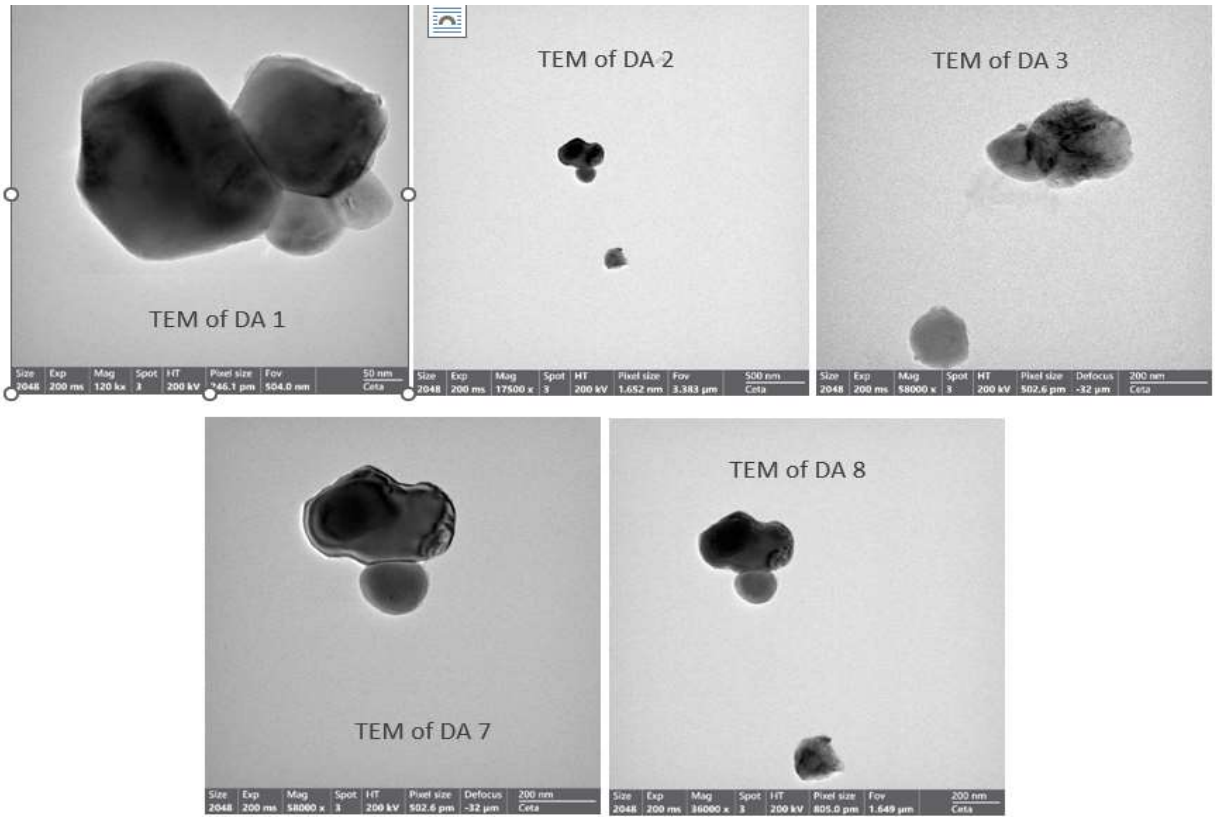


Figure 9 TEM images of various dispersing agents (DA 1,2,3,7and 8).

The durability of the printed and cured cotton fabric samples was evaluated by measuring their resistance to washing and rubbing. The Rota wash Colour fastness tester was utilized to evaluate the wash-fastness. Every fabric sample that was printed and treated, including a strip of multiple fibres, underwent a washing process of 30 minutes at 60°C in a solution consisting of 4 g/L regular detergent and 1 g/L sodium carbonate mixed in water at a 50:1 ratio. As per ISO 105 C06 guidelines, this holds true [7,43,52.53]. Rub-fastness tests were conducted utilizing the BYK crock meter. Every fabric sample that was printed and treated underwent a rub-fastness examination using both dry and moist cotton lawn rubbing cloth, performing ten back and forth rubs. according to the standard test. Drawing upon the findings of the washing and crock fastness outcomes, as presented in Table 7.

Table 7 Fastness obtained results for the printed samples

Sample Name	Sample Code	Washing fastness	Crock fastness	
			Dry	Wet
White 15% W 190	DA 1	4-5	3-4	4
White 15% W 755	DA 2	4-5	4	3-4
White 15% W 757	DA 3	4-5	3-4	3
White 15% W 4560	DA 7	3	2	1-2
White 15% W ES	DA 8	3-4	4	3-4

A wash fastness rating of 4-5 demonstrates that the dispersant remains fully absorbed within the cotton fibres and does not migrate throughout the fabric. According to the first image, the fastness of crocking produces remarkable outcomes in the range of 3 to 4, signifying complete integration of TiO2 pigment with cotton fibres. The exceptional dispersing ability of DA8 dispersing agents allowed this to be achieved, as opposed to standard DA1 or DA3 agents.

4. Conclusion

We developed a home-made dispersing agent for water-based titanium dioxide inkjet inks by creating a prepolymer through the chemical reaction between glycerol mono oleate (GMO) and toluene di isocyanate (TDI). The prepolymer was then reacted with gallic acid and terminated with succinic anhydride modified polyethylene glycol PEG 600. We assessed the performance of the resulting dispersant against a commercial dispersant by examining its zeta potential, viscosity dynamic surface tension, particle size, and TEM in titanium dioxide inkjet ink formulations.

The study revealed that GMO-gallic acid-succinic anhydride modified PEG 600 dispersant DA8 give particle size distribution (0.425 µm) compared to that obtained by the global dispersant DA1 (0.475 µm). i.e., had a 101% efficiency surpassing global dispersants for pigmented inkjet inks. also showed

comparable results in other properties, making it compete the effective dispersants for this kind of inkjet inks.

The research examines cotton that has been printed with inks specifically developed for wash and Crock Fastness, and the findings show similar outcomes to the inkjet ink often used for printing fabrics.

5. Conflict of interest

We confirm that there is no conflict of interest.

6. Acknowledgements

I would like to extend my sincere thanks and appreciation to my professors in the Department of Chemistry, Faculty of Science, Al-Azhar University

ESNA Chemicals Company deserves a lot of appreciation for providing their valuable assistance and support.

In addition, I would like to express my gratitude towards my colleagues at ESNA Chemicals, who have been tremendously supportive and helpful.

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