

Effect of Different Surfactant Monomers on Alkali-Soluble Emulsion Polymer as a Binder for Water Based Printing Inks

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IN THIS study hydrophobicallyalkali-soluble emulsion HASE was prepared by using semi batch emulsion polymerization technique and evaluated as a binder for water based printing inks. HASEwas prepared by using vinyl acetate and methyl methacrylate as hydrophobic monomers in addition to methacrylic acid as a hydrophilic monomer. Besides, anionic and nonionic emulsifiers are used and sodium persulfate as initiator. Three types of surfactant monomers are prepared by esterification of an acid or an anhydride with nonionic surfactant and then, the chemical structures were characterized using FT-IR spectroscopy. Each surfactant monomer was used in different ratios to prepare the emulsion polymer. However a sample without using surfactant monomer was prepared for comparison. The prepared HASE was diluted and then neutralized by using mono ethanol amine till pH from 8 to 9. Neutralized polymer solution was mixed with pigment dispersion and then applied on paper sheet and color strength was measured. The best final polymer latex was characterized by FT-IR, DSC, and TEM. The prepared polymer showed advanced behavior compared with commercial binder in water based printing ink formulations. The results obtained revealed that uses of 5g of surfomer in polymerization of HASE enhance the color strength and gravimetric conversion and reduce the precipitate and viscosity.

Keywords: Emulsion polymerization, Alkali soluble emulsion, Surfomer, Printing inks.

Introduction

Inks play an important role in our daily lives. In about 2500 Before Christ, writing inks were first manufactured in both ancient Egypt and China. Printing was invented by Chinese who used a mixture of colored earth, soot and plant matter for pigments, again mixed with gums as a binder. Today's printing inks are consisting of pigment, binder, solvent and various additives such as drying and chelating agents. Pigments that color the ink and make it opaque, resins that bind the ink together into a film and bind it to the surface, solvents that make the ink flow so that it can be transferred to the printing surface, additives that alter the physical properties of the ink to suit different situations[1].

The environmental and health problems caused by the inks containing volatile organic compounds (VOCs) required new solutions in printing chemistry and technology [2].

Films of polymer obtained from latex dispersions have been studied broadly over the past years. Especially over the last decade regulations to protect the environment have caused retreat from solvent-borne to water-borne systems, making a large amount of basic research in the field of latex dispersions. Emulsion polymerization is the key synthesis route for latex dispersions and emulsion polymer play an important role in numerous regions, particularly in architecture or decorative materials and in printing inks. These latex dispersions are prepared by batch or semi batch process using acrylic or styrene/acrylic monomers[3].

Acrylate dispersions have an excellent brightness and ageing resistance and are less odorous[4].

It is essential for good printability of the ink, especially in flexo and gravure processes printing at high press speed, printing process must be carried out without the ink drying in the

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cell of gravure cylinder. In water based emulsion polymer, however, the film formation process proceeds in different manner which adversely influences reversibility.

Besides very good reversibility, HASE exhibit excellent ink properties such as good pigment wetting, excellent compatibility and low minimum film forming temperature[3].

HASE is an essential ingredient in water based inks as it provides the required rheology, pigment wetting, and resolubility, and prevents drying of ink in the cylinders[5].

HASE polymer can be defined as a hydrophobically modified polyelectrolyte. When neutralized in aqueous solution with suitable base, the latex particles are be ionized as a result of the acid-base reaction [6].

Polymerizable surfactants act in emulsion polymerization both as a surfactant and a comonomer. Usually, emulsion stabilization is their main purpose, and the ability of copolymerization is an added advantage. Uses of surfomer reduce the purification step after polymerization, which is necessary when using traditional surfactants. Polymerizable surfactant simply builds into polymer structure and does not keep on reaction mixture. It also prevents migration of a surfomer to the interface (polymer/air and polymer/substrate) informed film of the lattice. Uses of surfomer result better properties of the coating, which reduces water sensitivity, and enhance adhesion, and gloss[7].

Surfomer consists of three parts: a hydrophobic part; a hydrophilic part and apolymerizable part usually with double bonds.

Polymerizable surfactants usually have various polymerizable moieties. Most common moieties are acrylic/ meth acrylic[8], vinyl benzyl [9] and Maleic anhydride[10].

A great advantage of maleic-based surfomers is the fact that they do not enter homo polymerization, but copolymerize with most vinyl monomers[11].

The synthesis of new maleic and methacrylic surfomers containing different polymerizable part is described. They were used for the evaluation of radical emulsion polymerization of Methyl Methacrylate (MMA), Vinyl Acetate (VAM), and Methacrylic acid (MAA) in the presence of sodium per sulfate (SPS) as an initiator. *Special Egypt.J.Chem.* **62**, No. 1 (2019)

attention was focused on the effects of surfomer type and concentration on the polymerization process and final properties of latex. In this study, HASE is prepared and its properties are enhanced by using surfactant monomer.

Materials and Methods

Materials

Industrial grade of Methyl Methacrylate (MMA), Vinyl Acetate (VAM), and Methacrylic acid (MAA) were supplied by Dow Chemical Company.

Maleic anhydride (MAn) was supplied by Excel chemical corporation (Taiwan)

Sodium luryl ether sulfate (Texapon) was supplied by Dow Chemical Company.

C₁₃ alcohol polyethylene glycol ether 6 ethoxylate (TRIDAC ISO-6), and C16-C18 alcohol polyethylene glycol ether 50 ethoxylate (ALCS 100) were supplied by Sasol (Europe).

Sodium persulfate (initiator) was supplied by NBM Chem. Company (England)

Para toluene sulfonic acid (PTS), and ME Hydroquinone (HQ) were supplied from Oxford lab chem.

Blue pigment dispersion supplied by ABC Company (Egypt).

Mono ethanol amine (MEA) was supplied from SIGMA ALDRICH.

Synthesis

Synthesis of surfomer

In 1000 ml 3 neck flask equipped with magnetic stirrer, condenser, and thermometer, the amount of TRIDAC ISO-6 was charged to the flask. The temperature was raised to 70°C by using heating plate, and the stirring rate was adjusted at 200 rpm., then a mixture of meth acrylic acid (MAA) (or malic anhydride) and hydroquinone were added. HQ was added to prevent polymerization of meth acrylic acid by the effect of high temperature of esterification. Para toluene sulfonic acid was added as catalyst when the temperature reached to 100°C. The temperature was raised to 110°C and held at (105-115 °C) for 2 h. After 2 h the liberation of water was stopped and the product was cooled, discharged and filtered. The amounts of TRIDAC ISO-6, methacrylic, maleic anhydride, hydroquinone, and para toluene sulfonic acid are listed in Tables 1&2.

*Surfactant monomer formulation***TABLE 1. Surfactant monomer of methacrylic acid with TRI DAC ISO-6 formulation.**

Surfmer code	Component	Tridaciso6	MAA	PTS	HQ
SM 1	Amount (g)	464	86	4	0.2

TABLE 2. Surfactant monomer of malic anhydride with TRI DAC ISO-6 formulation.

Surfmer code	Component	Tridaciso6	MAAn	PTS	HQ
SM 2	Amount (g)	464	98	4	0.2
SM 3		464	49	2	0.1

*Synthesis of HASE poly acrylate binder**a- Preparation of pre-emulsion*

In 1000 ml glass container 53.3% of total distilled water, 70% of total anionic emulsifier, and then total amount of nonionic emulsifier were added. The previous amounts were mixed and dissolved by using high speed mixer (1000 rpm for 10 minutes).

Hydrophilic monomer (methacrylic acid) was added gradually during high speed mixing. And then hydrophobic monomers were added during high speed mixing (2000 rpm). The previous mixture was stirred for more 15 minutes.

b- Preparation of reactor content

In 2-liters 3-necked flask equipped with mechanical stirrer, condenser, thermometer, and water bath, 40% of total water amount and 30% of total anionic emulsifier amount were added at room temperature and stirred for 5 minutes at 80-85°C.

c- Preparation of initiator solution

The total amount of initiator was dissolved in 6.7% of total water. Chemicals are listed in Table 3.

d-Polymerization process

1- The stirring rate of reactor was adjusted at

TABLE 3. Emulsion polymer formulation.

Component run	VAM (g)	MMA (g)	MAA (g)	SM ₁ (g)	SM ₂ (g)	SM ₃ (g)	Tex (g)	ALSC 100(g)	H ₂ O (g)	I (g)
A	150	150	100	-	-	-	30	12.5	750	2.4
B1	150	150	100	5	-	-	30	12.5	750	2.4
B2	150	150	100	10	-	-	30	12.5	750	2.4
B3	150	150	100	15	-	-	30	12.5	750	2.4
B4	150	150	100	20	-	-	30	12.5	750	2.4
B5	150	150	100	25	-	-	30	12.5	750	2.4
C1	150	150	100	-	5	-	30	12.5	750	2.4
C2	150	150	100	-	10	-	30	12.5	750	2.4
C3	150	150	100	-	15	-	30	12.5	750	2.4
C4	150	150	100	-	20	-	30	12.5	750	2.4
C5	150	150	100	-	25	-	30	12.5	750	2.4
D1	150	150	100	-	-	5	30	12.5	750	2.4
D2	150	150	100	-	-	10	30	12.5	750	2.4
D3	150	150	100	-	-	15	30	12.5	750	2.4
D4	150	150	100	-	-	20	30	12.5	750	2.4
D5	150	150	100	-	-	25	30	12.5	750	2.4

All ingredients were in gram.

150 rpm and temperature was raised to 80-85°C.

2- The pre-emulsion and initiator solution were added simultaneously during polymerization period (4 hours).

3-The polymerization content is stayed at the polymerization temperature for an hour to ensure high percentage of monomer conversion.

4-The flask content was cooled to 40°C, discharged, filtered and the precipitate was collected and weighed.

e- Neutralization process

25 parts of prepared emulsion were added to 75 parts of distilled water, mixed and then neutralized by using mono ethanol amine to pH (8-9).

f- Ink preparation process

40 parts of alkali soluble emulsion solution were added to 10 parts of pigment dispersion (Table 4) and applied as film on white paper by using analog film applicator for inks.

Methods

FTIR spectra

The chemical composition of an emulsion polymer sample and surfactant monomer can be determined by Fourier transform infrared (FTIR) spectroscopy. FTIR spectrum in the region from 4000 to 500 cm^{-1} was recorded for a sample prepared by making a film of the latex on a glass plate and drying it, and then removing the film from the glass and testing it by using TENSOR 27

Mid FT-IR spectrophotometer made by BRUKER Optics Ettlingen-Germany

Thermal analysis

The thermal stability of polymer sample was determined by DSC using NETZSCH STA 409 C/CD instrument in the range of 20-1000 °C with heating rate 10 k/min in He atmosphere where the crucible used was DSC/TG pan Al_2O_3 .

Solid Content and Gravimetric Conversion

The emulsion polymer was dried to a constant mass at temperature 130 °C (see, for example, ISO 1625) and the solids content is then expressed as the percentage ratio of the dry matter to the total mass of the sample.

Theoretical solid content % =

$$\frac{\text{total introduced solid}}{\text{total weight}} \times 100$$

Actual Solid content % =

$$\frac{(\text{weight after drying}) * 100}{\text{weight before drying}}$$

Gravimetric Conversion =

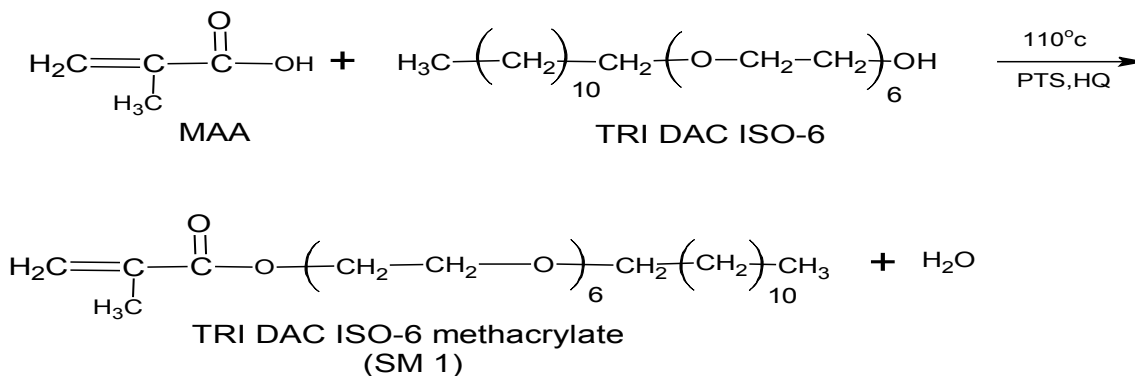
$$\frac{\text{Actual Solid content \%}}{\text{Theoretical solid content \%}}$$

Viscosity

One part of polymer latex was added to three parts of water and neutralized to pH 8-9 and then viscosity is measured by using RV-D brook field viscometer.

TABLE 4. Ink formulation.

Component	Polymer	H ₂ O	MEA	Pigment
Amount (g)	10	30	Drops up to pH(8-9)	10



sample is D₁.

D1 sample is characterized by:

FTIR spectroscopy of the prepared copolymer D1 Polymer structure

As shown in Fig. 4, FTIR spectrum of the copolymer of vinyl acetate, methyl meth acrylate and meth acrylic acid in the region from 4000 to 400 cm⁻¹ was recorded sample give band at 3423 cm⁻¹ that is characteristic of hydroxyl [OH] group of meth acrylic acid, band at 1704cm⁻¹ that is characteristic of ester or carboxyl [C=O] group of methyl meth acrylate, vinyl acetate or meth acrylic acid, band at 1180 cm⁻¹ that is characteristic of ether [C-O] group of ethoxylate groups and give band at 2930 cm⁻¹ that is characteristic of aliphatic [CH] groups.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC)

As shown in Fig. 5, Thermal gravimetric analysis of D₁ polymer sample illustrate that the prepared polymer is stable up to 280 °C and it is suitable for use in high temperature drying printing machines.

Figure 6 showed the stages of DSC decomposition temperature: initiation stage at 250°C, peak temperature 336.49°C and final temperature at 450°C. the knowledge of degradation and mode of decomposition under the influence of heat is highly recommended for the

process parameter. the threshed decomposition temperature gives an indication of the highest processing temperature that can be used.

Morphology of the polymer (Transmission electron microscope) (TEM)

As shown in Fig. 7, TEM image shows that the diameters of most particles of D₁ between 64 & 104nm with narrow distribution, all particles have honey-cell shape. Stability of prepared polymer was not mentioned, because of hydrophobically alkali soluble emulsions are freeze/thaw unstable. And that zeta potential studying is not important. [12]

Studying the Optimization effect of surfactant monomers on the prepared polymers

Effect of surfomer type and amount on the precipitate amount

As shown in Fig. 8, precipitated polymer amount was affected by the type and the amount of surfactant monomer (SM).

When we used TRI DAC ISO-6 methacrylate surfactant monomer (SM₁) the amount of precipitate was constant value (increasing of SM amount up to 25 g not affect the precipitate amount) [13]. On the other hand, TRI DAC ISO-6 mono maleate (SM₂) and TRI DAC ISO-6 di maleate (SM₃) affect the precipitate which increases the amount of SM lead to increase the precipitate amount.

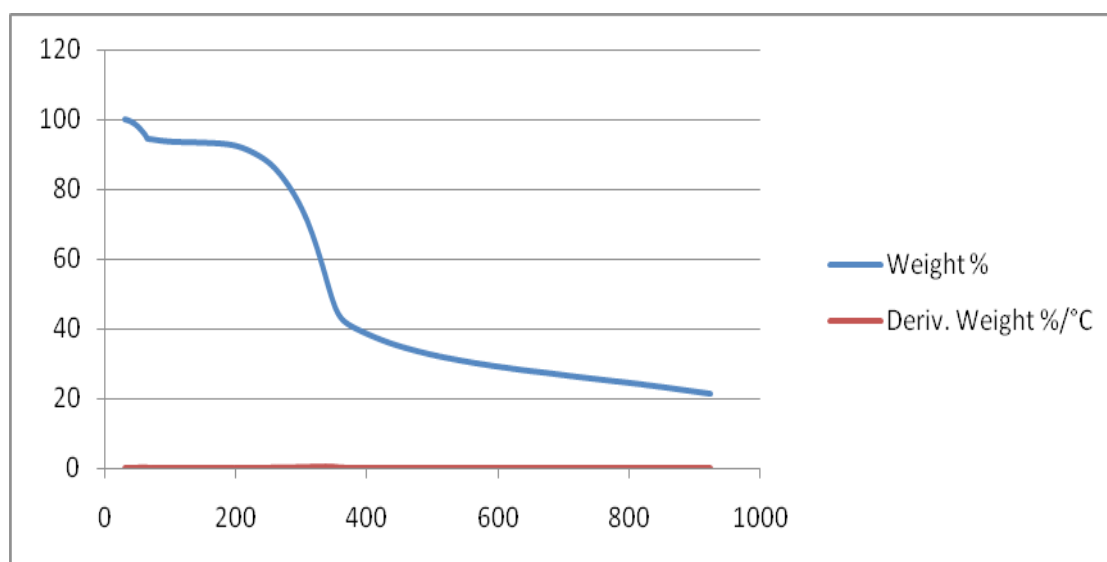


Fig. 5. TGA of polymer sample(D1).

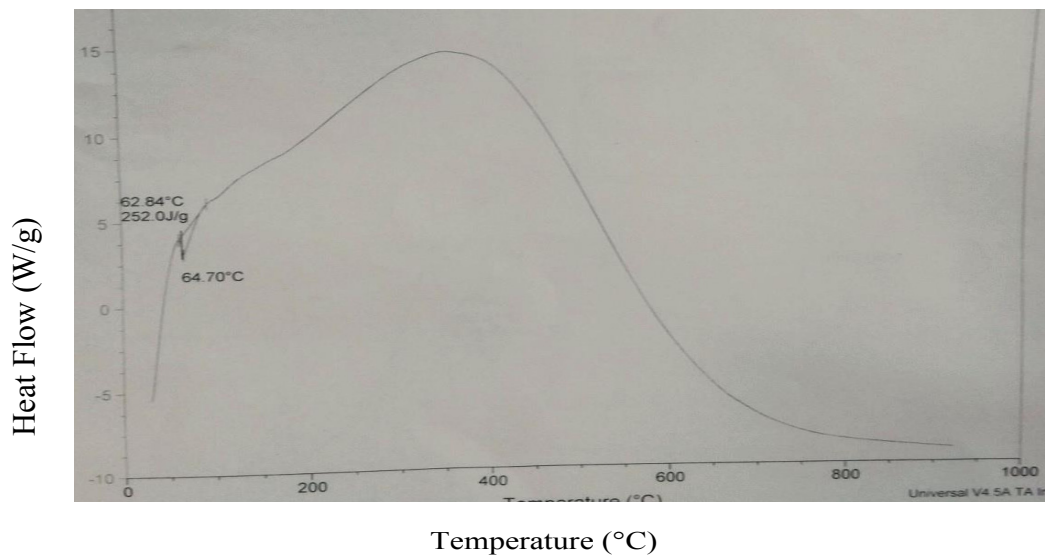


Fig. 6. DSC of polymer sample (D1).

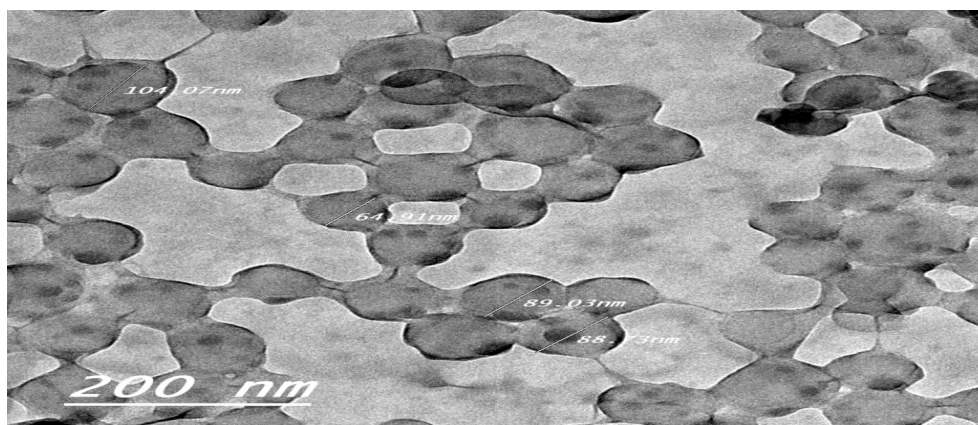


Fig. 7. TEM of polymer sample (D1).

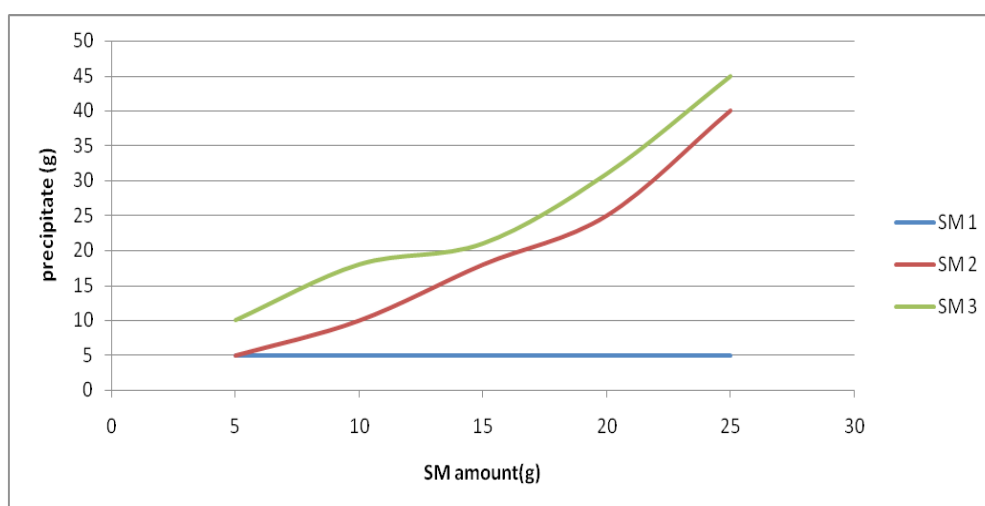


Fig. 8. Effect of the type and amount of surfamer on the precipitate yield.

The highest value of precipitate (45 g) was obtained when 25 g of SM₃ was used. While 40 g of precipitate was obtained when 25 g of SM₂ was used. The increase in the precipitate can be explicated by instability of produced polymer particles and or polymerization out of micelle is take place.

Effect of surfomer type and amount on the gravimetric conversion

In polymerization process gravimetric conversion is referred to the polymer yield from the total amount of monomers and it is an important factor in emulsion polymerization industry.

As the results shown in Fig. 9, gravimetric conversion percent was constant value (98.7%) when SM₁ was used, this value was the maximum percent which the maximum rate of polymerization is obtained when SM₁ was used. whereas gravimetric conversion percent decreases when the amount of SM₂ and SM₃ increases. Gravimetric conversion is reached to 90% and 88.3% when 25 g of SM₂ and SM₃ is used respectively. This means that using of high percent of SM₂ and SM₃ hinders polymerization process and decrease the rate of polymerization, because of large number of surfomer molecules

(long chain molecules) are built in the wall of micelle and prevent the penetration of live radicals into micelle.

Effect of surfomer type and amount on the viscosity

The Viscosity of binder is important property which affects the final viscosity of ink and makes it applicable or not applicable. As discussed in many papers surfactant monomer support the viscosity of final polymer. In this work, all prepared surfactant monomer increase the viscosity. The highest value of viscosity is obtained (15300 cPs) when SM₁ is used. In this case binder is acting as thickening agent. As Fig. 10 shows lowest value of viscosity is obtained when SM₃ is used. Viscosity increases by increasing the amount of all types of SM.

Effect of surfomer on the color properties of printed sample

Color strength of printed samples is strongly depending on the type of binder which is responsible for transfer of color to substrate[14].

In general, using of SM increases the color strength in comparison with prepared sample without SM, and commercial standard sample (EOC 4118).

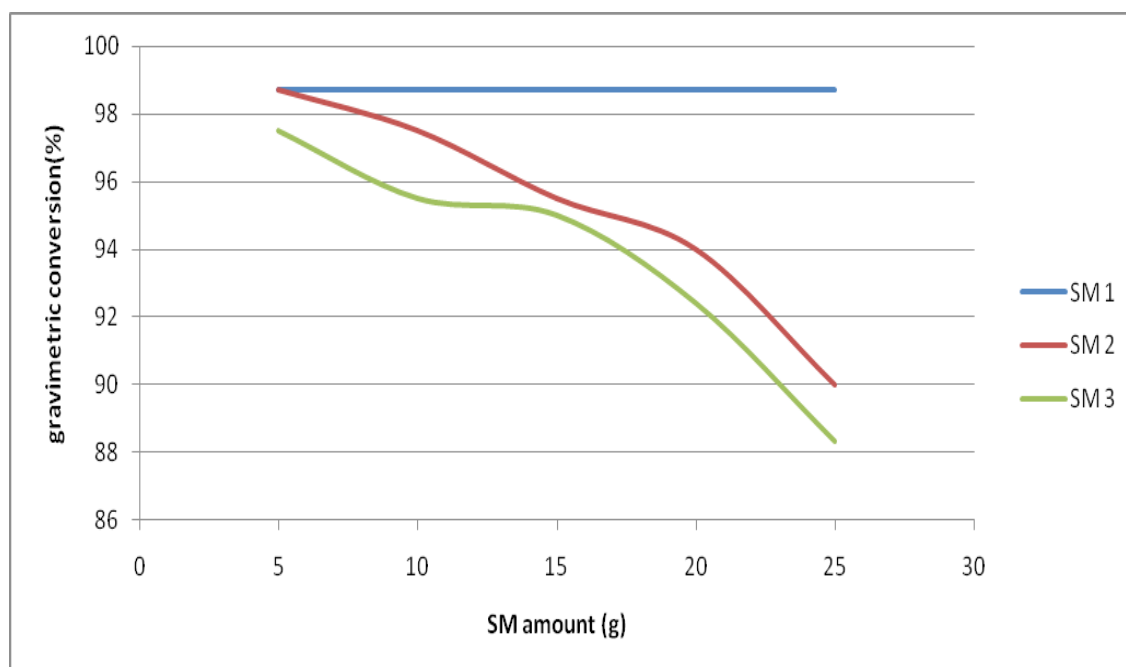


Fig. 9. Effect of the type and amount of surfomer on the gravimetric conversion.

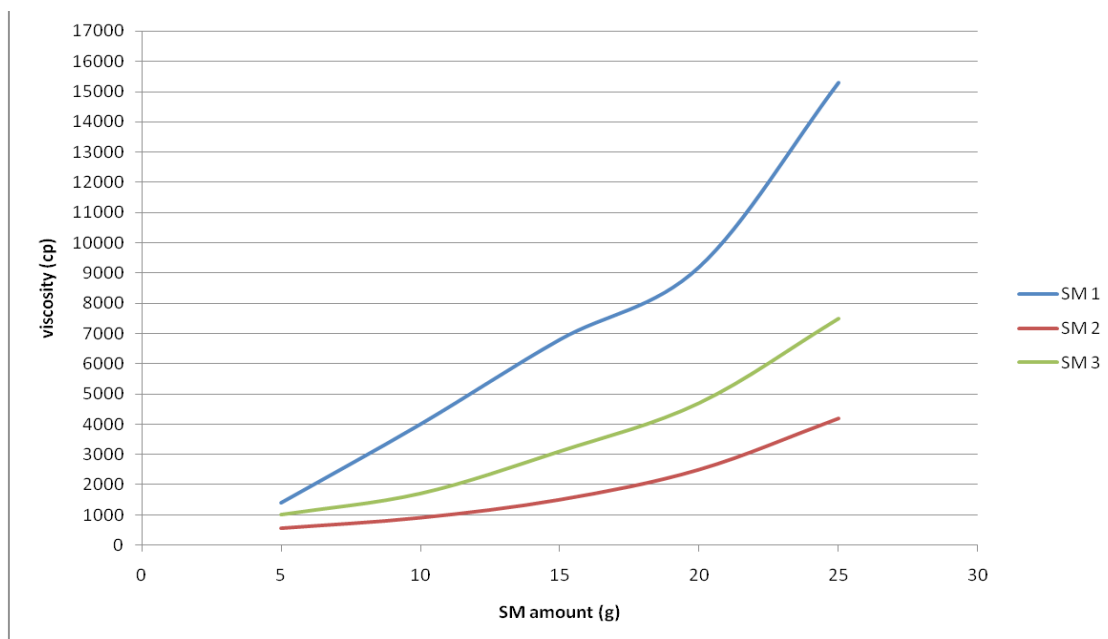


Fig. 10. Effect of the type and amount of surfomer on the viscosity.

The best three polymer samples in the three SM series are selected according to the highest gravimetric conversion, and the lowest precipitate percent and viscosity. The best three polymer samples are compared with A sample and commercial standard sample in printing ink application (Fig. 11).

The color measurements were determined on a Hunter Lab Ultra Scan PRO spectrophotometer with a D65 illuminant and 10° standard observer. The L axis runs from top to bottom. The maximum for L is 100, which would be a perfect

reflecting diffuser. The minimum for L would be zero, which would be black. The a and b axes have no specific numerical limits. Positive a is red. Negative a is green. Positive b is yellow. Negative b is blue[15]

As shown in Fig. 12, SM effects positively on the color strength. The color strength of sample A is less than the color strength of other samples. On the other hand D1 is better than another sample which L factor is the smallest value (43.19).

Values of L factor for B_1 and C_1 indicate that, uses of SM_1 and SM_2 affects partially positive on

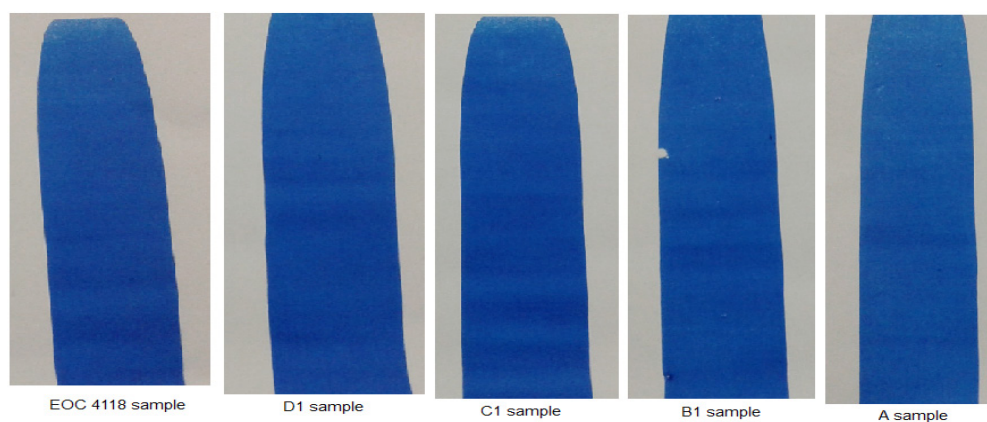


Fig. 11. Printed ink samples.

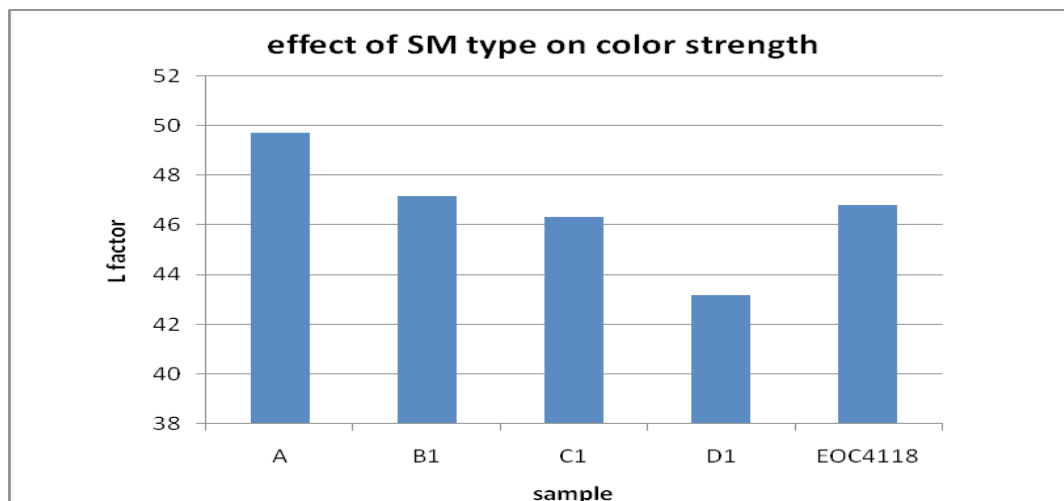


Fig. 12. Effect of surfomer type on the color strength (L factor).

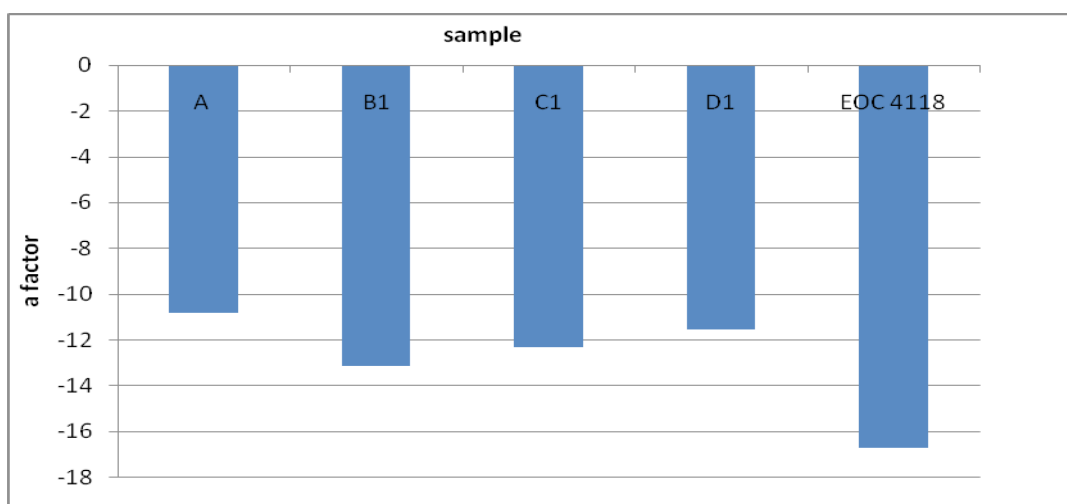


Fig. 13. Effect of surfomer type on the red/green coordinate (a).

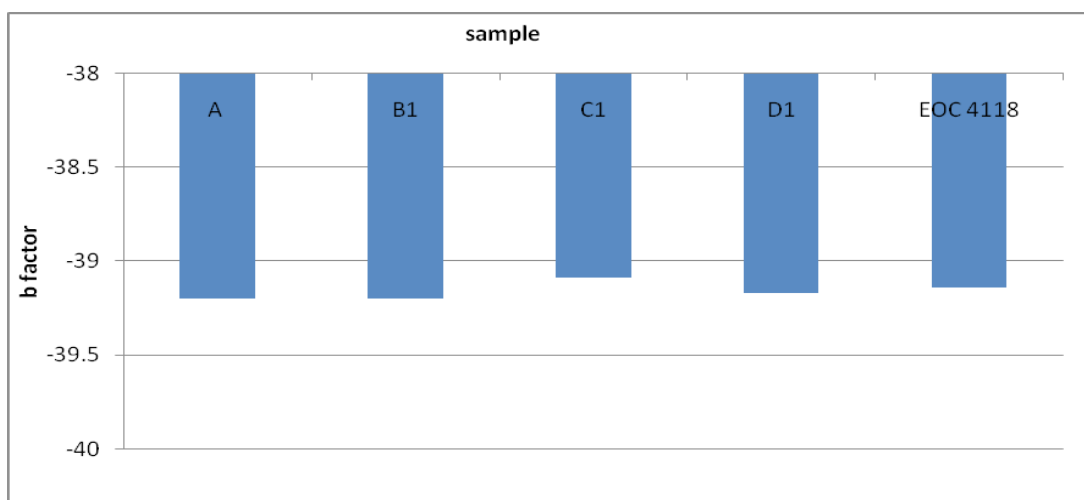


Fig. 14. Effect of surfomer type on the yellow/blue coordinate (b).

color strength.

Figures 13 and 14 show that color direction is not affected by the type of surfomer.

Conclusion

Synthesized methacrylate surfomer enhance the viscosity of polymer, and slightly affect the color strength of printing process. Synthesized di maleate surfomer enhance the color strength of printing process, and slightly affect the viscosity. Methacrylate surfomer can be polymerized better than maleate surfomer in emulsion polymerization. The highest gravimetric conversion, and color strength, and the lowest precipitate percent, and viscosity are obtained when 5g of TRI DAC ISO-6 di maleate (SM3) is used.

References

1. Kirth-Othmer, *Encyclopaedia of Chemical Technology* (3rd Edition), V.13 (374-397) & V.19 (110-175), Wiley & Sons, New York (1981).
2. Michel B., Bernard A., Bitesh A., Dalamache E., Geissla M., Junchery D., Renaut J.P., Rothizer H., Schimdt H., Schmidt P., Stutz R., Wolf H., Printing meets Litho: Soft approaches to high resolution patterning. *IBM Journal of Research & Development*, **45** (8), (2001).
3. Peters A., A new generation of water-borne ink binders for packaging films and paper (Part I). *Surface Coatings International Part B: Coatings Transactions*, **84** (3), 189-195 (2001).
4. Hermann, Wesslau, Spoor Herbert, Pohlemann Heinz, Addicks Guenther and Reinbold Immo, Binders for paper coating compositions. *U.S. Patent* 3,365,410, issued January 23 (1968).
5. Wu, Wenjun, Steve Severtson and Christopher Miller, Alkali-soluble resins (ASR) and acrylic blends: influence of ASR distribution on latex film and paint properties. *Journal of Coatings Technology and Research*, **13** (4), 655-665 (2016).
6. Jiménez Regalado, Enrique Javier, Claudia Cecilia Rivera Vallejo, Hortensia Maldonado Textle, Ramiro Guerrero and Jorge Félix Espinosa Muñoz, Influence of Hydrophobe, Surfactant and Salt Concentrations in Hydrophobically Modified Alkali-Soluble Polymers Obtained by Solution Polymerization. *Journal of the Mexican Chemical Society*, **56** (2), 139-143 (2012).
7. Guyot, A.I. and Tauer K., Reactive surfactants in emulsion polymerization. *In Polymer Synthesis*, pp. 43-65. Springer, Berlin, Heidelberg (1994).
8. Samakande, Austin, Patrice C. Hartmann, Valeska Cloete and Ronald D. Sanderson, Use of acrylic based surfimers for the preparation of exfoliated polystyrene-clay nanocomposites. *Polymer*, **48** (6), 1490-1499 (2007).
9. Chudej J., Guyot A. and IgnácCapek, Dispersion copolymerization of styrene with vinylbenzyl-terminated polyoxyethylenemacromonomer."In *Macromolecular Symposia*, Vol. **179** (1), pp. 241-256. Weinheim: WILEY-VCH Verlag GmbH, (2002).
10. Abele S., Graillat C., Zicmanis A. and Guyot A., Hemiesters and hemiamides of maleic and succinic acid: synthesis and application of surfactants in emulsion polymerization with styrene and butyl acrylate. *Polymers for Advanced Technologies*, **10** (6), 301-310 (1999).
11. Chevalier Yves, New surfactants: new chemical functions and molecular architectures. *Current Opinion in Colloid & Interface Science*, **7** (1-2), 3-11 (2002).
12. Lesota S., Hydrophobically modified alkali-soluble as thickeners for exterior latex paints. *Polymers in aqueous media: performance through association* 546-549 (1989).
13. Abdel-Wahhab H., Naser A. M., Abdel-Hai F., Mohamed Sh I. and Abdel-Hakim A., Preparation and Evaluation of Hydrophobically Modified Alkali-Swellable Emulsion (HASE). *Journal of Applied Sciences Research* **7** (9), 1386-1394 (2011).
14. Yaman N., Ozdogan E. and Seventekin N., Improvement Fastnesses and Color Strength Of Pigment Printed Textile Fabric. *Journal of Engineered Fabrics & Fibers (JEFF)*, **7** (2), (2012).
15. Markovic, Ivana, Jelenallic, Dragan Markovic, Vojislav Simonovic, and Nenad Kosanic, Color measurement of food products using CIE L* a* b* and RGB color space. *J. Hyg. Eng. Des* **4**, 50-53 (2013).

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تأثير العوامل ذات النشاط السطحي القابلة للبلمره المختلفه على البوليمرات المستحلبه الذائبه بتأثير القاعده المستخدمه كماده رابطه فى احبار الطباعة ذات الاساس المائى

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فى هذه الدراسة تم تحضير بوليمرات مستحلبه تذوب بتأثير القاعده بطريقه البلمره الاستحلابيه. وتم تقييم البوليمرات الناتجه فى احبار الطباعة ذات الاساس المائى. تحضر البوليمرات باستخدام خلات الفينيل و ميثيل ميثا اكريلات كمونومرات لا تذوب فى الماء بالاضافه الى ميثا اكريليك اسيد كمونومر يذوب فى الماء. يستخدم فى عمليه التحضير عامل مستحلب انيونى وغير ايونى ويستخدم صوديوم بير سلفات كبادئ للتفاعل.

تم تحضير ثلاثه انواع من العامل المستحلب القابل للبلمره عن طريق أسترة حمض او انهيدريد مع عامل مستحلب غير ايونى و يوصف ب FT-IR.

تم تحضير بوليمرات بنسب مختلفه من كل عامل مستحلب قابل للبلمره و تحضير ايضا بوليمر بدون عامل مستحلب قابل للبلمره للمقارنه فى الطباعة.

تم تخفيف البوليمرات المحضرة بالماء و معادلتها باستخدام مونو ايثانول أمين الى pH من ٨ الى ٩ ثم الخلط مع المخضب وطباعتها على ورق ابيض.

تم طباعة أفضل ثلاث عينات من البوليمرات المحضرة باستخدام العوامل المستحلبه القابله للبلمره مقابل عينه محضرة بدون استخدام عامل مستحلب قابل للبلمره و عينه قياسيه. تم توصيف أفضل عينه بوليمر ب FT_IR و DSC و TEM والتي أظهرت نتائج متقدمه بالمقارنه مع عينه قياسيه.