NC STATE
College of Textiles

JTATM
Journal of Textile and Apparel,
Technology and Management

Volume 10, Issue 1, 2016

Novel Synthesis of Nano-emulsion Butyl Methacrylate/Acrylic Acid via Micro-emulsion Polymerization and Ultrasonic Waves

Naglaa S. Elshemy[1], Ahmed G. Hassabo[2], Zain M. Mahmoud[1] and Karima Haggag[1]
[1]National Research Centre, Textile Research Division, Dyeing, Printing and Textile Auxiliaries Department
[2]National Research Centre, Textile Research Division, Pre-treatment and Finishing of Cellulosic Fibers Department, Dokki, Giza, Egypt
aga.hassabo@hotmail.com

ABSTRACT

Micro-emulsion and emulsion polymerization can have some similarities in starting conditions and polymerization mechanism, but the resulting nano-emulsion is unalike in particle size and molecular weight. The purpose of this research is to prepare nano-emulsion co-polymer particles based on butyl methacrylate/acrylic acid (BMA/AAC) with high monomer/surfactant ratio by using Ultrasonic homogenizer. The nano-emulsion co-polymerizations processes were carried out with different AAC/BMA ratio and different modified process. Sodium dodecyl sulphate (SDS) and potassium peroxy disulphate /glucose were used as emulsifier and redox initiator, respectively. The prepared nano-emulsion was characterized via spectroscopic measurement, FT-IR, particle size analyzing, GPC, transmission electron microscope (TEM), and glass transition temperature (Tg). The prepared nano-emulsion showed that, the particle size and homogeneity of the prepared nano-emulsion are depend on monomers ratio and preparation method. TEM analysis showed that the nano-emulsion had a number-average particle diameter less than 50 nm and with narrow particle size distribution. It was also found that the glass transition temperatures (Tg) of the film formed from the nano-emulsion could be lower than −40□C. The study involved the application of the prepared nano-emulsion as binder for pigment printing process onto cotton fabric by using a flat screen technique and the prints were dried and thermal cured. The printed fabrics were evaluated according to standard test methods to determine if the addition of prepared nano-emulsion to print pastes yielded equivalent or improved performance properties. Results showed that the prepared nano-emulsion has excellent fastness to washing, perspiration, and light but slightly lowered to Rubbing and made the fabrics slightly stiffer. A benefit of the prepared nano-emulsion was that it slightly increased the viscosity of many of the print paste formulations and reduced the amount of thickener that was needed.

Keywords: Micro/nano-emulsion, co-polymer, binder, textile printing, pigments, textile technology, Energy efficiency and ultrasonic waves

1. Introduction

These days, there is a great attention in the design of nanoparticle materials as they were discovered to give several features attributable to their small size and high surface to volume ratio. (Niemeyer, 2001) In this framework, aquatic suspensions of functionalized polymer nanoparticles, so called ‘nano emulsion’, grasp most pledge for the progress of new polymer supports alongside enhanced revealer attention. (Amigoni-Gerbier, Desert, Gulik-Kryswicki, & Larpent, 2002; Amigoni-Gerbier & Larpent, 1999; Larpent, 2003) Within existence technology, polymer nanoparticles were discovered to give important helps for the design of carrier, binder or investigations, which can be well suited for intracellular transport and innate measurements (Davda & Labhasetwar, 2002; Kumer, Wolfbeis, & Klimant, 2002; Lu & Rosenzweig, 2000; Park, Brasuel, Behrend, Philbert, & Kopelman, 2003; Sumner, Aylott, Monson, & Kopelman, 2002)

During the last ten years, there have been a large number of researches, which focused on nano composite materials. Many researches have appeared in various fields such as metals, ceramics, semiconductor nanoparticles, and polymer related nano-structured materials, as an example, the polymer/metal (or semiconductor), nano-composite. (Chow & Gonsalves, 1996; Jena & Behera, 1996; Moser, 1996)

However, until recently there were very few description (De & Robinson, 2004; Stupp et al., 1997) from the direct synthesis of the polymer nano-particles (especially with diameters less than 20 nm), that is allowed to be used in a variety of purposes.

Textile industry is under tremendous pressure from international competition. There is an urgent need for new technologies to keep the industry competitive.

J T A T M

Cellulosic fibers are natural polymers of vegetable origin, like cotton, linen, jute, ramie, hessian and sisal. (Mohamed & Hassabo, 2015; Visakh & Arao, 2015) Therefore, it would be useful to impart high performance properties to natural fibers. (El-Zawahry, Abdelghaffar, Abdelghaffar, & Hassabo, 2016; Hassabo, 2014; Hassabo, Mendrek, Popescu, Keul, & Möller, 2014; Hassabo & Mohamed, 2016; Hassabo, Nada, Mohamed, & Abou-Zeid, Accepted for publication 2015; Hassabo, Schachschal, et al., 2014; Ibrahim, El-Sayed, Fahmy, Hassabo, & Abo-Shosha, 2013; Mohamed, El-Naggar, Shaheen, & Hassabo, 2016) There are several ways to functionalize the natural fibers e.g. deposition and/or infiltration of functional polymeric materials onto/into the fiber surface, (Abo-Shosha, Nassar, Haggag, El-Sayed, & Hassabo, 2009; Mohamed, Er-Rafik, & Moller, 2013a, 2013b; Waly, Abou-Zeid, Marie, El-Sheikh, & Mohamed, 2009; Waly, Marie, Abou-Zeid, El-Sheikh, & Mohamed, 2012) using nanotechnology while preserving the inherent properties of the fiber, to modify the fiber surface by applying a nano-coating. (Hassabo, 2011, 2014; Hassabo, Erberich, Popescu, & Keul, 2015; Hassabo, Mendrek, et al., 2014; Hassabo, Schachschal, et al., 2014; Mohamed, El-Sheikh, & Waly, 2014)

Ultrasound or ultrasonic energy, promises substantial rewards for the textile industry through advancements in two important area: a) decrease the manufacture cost (improved quality as well as speed of processing) and b) solution to environmental impact problems (reduce in total use of energy, water and processing chemicals).

Ultrasonic waves are sonic vibrations with a frequency up to 17 kHz - beyond the audible range of a human being. Ultrasonic waves including electromagnetic waves can be controlled to be reflected, refracted and focused, but they need a medium using elastic property for their propagation. When ultrasonic waves propagate, particles in the elastic medium oscillate and energy move through the medium in the propagation direction. The marked effects of ultrasound really arise from the way in which sound is propagated through the medium. These waves can be distinguished as:

- Longitudinal waves, in which the particles oscillate in a direction parallel to the wave propagation direction.
- Transverse or shearing waves, in which the particles oscillate in a direction perpendicular to the wave propagation direction.

In fact, both waves can be transmitted, while in gases and liquids only the longitudinal waves are transmitted. In liquids, longitudinal vibration of molecules generates a series of compressions and rarefactions, i.e., areas of high and low pressure. Cavitation is phenomena, which form a cavities or bubbles, can rise at low pressure in the rarefaction region. Cavitation process is depends on different factors such as the frequency, wave intensity, (Steele & Schiwall, 1959) liquid medium temperature, and its vapor pressure. This phenomenon is responsible for most of the physical and chemical effects that have been observed in solid/liquid and/or liquid/liquid systems. (Harvey, Gachagan, & Mutasa, 2014)

The main purpose of this study is to obtain a nano size binder with high monomer/surfactant ratio via a modified micro-emulsion polymerization process by using an Ultrasonic method (UM), and compared the result with the traditional method (TM). Also, investigated the use of the obtained nano emulsion as a binder in pigment print pastes for textiles.

2. Experimental

2.1. Materials

In this study Butyl methacrylate (BMA($C_6H_{14}O_2$), 99%, MW 142.20 g/mol, Merck Schuchardt OHG) was used, acrylic acid (ACA, 99.5%, MW 72.06 g/mol, PanreacSintesis), sodium dodecyl sulfate (SDS, 97%, MW 288.38 g/mol, Merck Schuchardt OHG) as emulsifier, potassium persulfate (KPS, 98%, MW 270.33 g/mol, Merck Schuchardt OHG) as initiator and Glucose (95%, MW 198.17, RFCL Limited). In all experiments, Deionized water were used.

Commercial pigment namely Gree 3GL and thickener Daicothick 1600 were supplied from DAICO for chemicals industry S.A.E.

Scoured bleached cotton fabric 100% (poplin) plain weave (140 g/m^2) which kindly supplied from Misr Co. for spinning and weaving, Mehalla El-Kubra, Egypt.

2.2. Ultrasonic stirring systems

Ultrasonic Homogenizing is a mechanical process was used to reduce particles in a liquid so that they become uniformly, small and evenly distributed. The optimum conditions for miniaturization obtained from Homogenizer were applied upon using the Ultrasonic stirrer (Sonics & Materials, Inc.), Model: VCX750, volts: 230 VAC 50/60 HZNOM, USA)

2.3. Synthesis of nano-size polymer

Nano-emulsion were synthesized through differential micro-emulsion polymerization (by two methods; a) Traditional method (TM) and b) Ultrasound method (UM)) as follow:

a. **Traditional method (TM):** in this method the KPS (0.2 g), SDS(5g), 0.1 g wt.% of glucose, 2 ml monomer (ACA) and 80.7 ml distilled water were put into a round-bottom flask (250 ml) with four-neck, equipped with a magnetic stirrer, condenser, thermometer and additional funnel. Keep it for 10 min at room temperature. Then raise temperature to 40°C with moderate stirring (250 rpm) for 20 minutes. Raise the temperature up to 70°C and keep it for 10 minutes. After that, the monomer was adding using additional funnel in a differential manner (continuously added in very small drops to avoid the aggregation polymerization, especially along the

J
T
A
T
M

wall of the flask) during 2 h, with moderate stirring (ca. 200 rpm, helps the homogeneity and stability of the micro-emulsion, to prevent aggregation and achieve a true emulsion). Keep the temperature and stirring for additional 2 h (total time 4 h and 30 min.).

b. **Ultrasound method (UM):** in this method the KPS (0.2 g), SDS (5 g), 0.1 g wt.% of glucose, 2 ml monomer (ACA) and 80.7 ml distilled water were added in to the reactor and left it to 10 min at room temperature, then add all the monomers to the reactor (18 ml.). The probe is turned to resonate at a specific frequency, (20 KHZ±100 HZ). The Ultrasonic stirrer was operated for 30 min. at 80°C. Then keep it with moderate stirring (ca. 200 rpm) without ultrasonic for another 30 min. The moderate stirring helps the homogeneity and stability of the nanolatex (total time 1 h and 10 min.)

2.3.1 Effect of monomer ratio

A mixtures of ACA/BMA was used using different ratio (100/0, 75/25, 50/50, 25/75, or 0/100 wt. %) and the other experimental conditions unchanged. The total monomer fraction of 20 wt. % in the emulsion (5 g wt. % SDS (based on total volume), 0.2 g wt.% of KPS, 0.1 g wt.% of glucose and 80.7 ml distilled water) were charged to the reactor and adapted the same procedure as the processes mentioned above for both methods.

2.3.1. Effect of emulsifier content

The emulsifier content (Sodium dodecyl sulfate (SDS)) was varied from (2-6 g) wt. %, and the other experimental conditions kept without change, and then repeat the same procedure mentioned above to prepare nano-emulsion.

2.3.2. Effect of initiator concentration

The initiator (KPS) content was varied from (0.1 - 0.4) g wt.%, to study the effect of initiator concentration on the particle size of the obtained nano-emulsion, in this step all other polymerization recipes were fixed and then repeat the same procedure mentioned above to prepare nano-emulsion.

2.3.3. Effect of total monomer content

Four experiments with various total monomer concentration of 5 - 20 wt. %, were applied to looking to the effect of total monomer content on the particle size of the obtained nano-emulsion, while all polymerization recipes were fixed.

2.4. Printing paste

Distilled water was used to prepare the printing paste with heavy stirring by adding 15-20 g/100 ml prepared binder by using UM and TM, separately, then 3 g/100 ml thickener, 0.5 g/100 ml diammonium sulphate and 4 g/100 ml urea were added. After that, 4 g/100 ml pigments was added to each printing paste; the paste was stirred for 10 minutes. The final print paste viscosity was 21,000 cps at rate of shear of 2.180 as determined with Brookfield Viscometer. (Haggag et al., 2012)

J
T
A
T
M

2.5. Printing technique

Each printing pastes were applied separately to 100% cotton fabrics using the flat screen printing method, dried at ambient temperature, to fix the color through the polymerization process, the goods were subjected to thermal cured (160°C for 4 minutes) in a thermal static oven (Mathis, Switzerland). The printed samples were subjected to washing, rinsing thoroughly with tap water, and then rinsing with warm water to remove the unfixed dye.

2.6. Characterizations

2.6.1. Glass transition temperature (Tg)

DSC measurements for measuring the glass transition (Tg), melting and the crystallization behavior of the substances were carried out on Netzsch DSC 204. The measurements were run using nitrogen flow at 20 ml/min as purge gas.

2.6.2. *Fourier transform infrared spectroscopy (FT-IR)*

Fourier transform infrared spectroscopy (FT-IR) was performed by using a Nicolet 6700 with (ATR Zn/Se) to determine the functional groups in the obtained nano-emulsion. Resolution for the infrared spectra was 4 cm^{-1} and there were 32 scans for each spectrum. The tester collected transmittance of the infrared in the film between 400 and 4000 cm^{-1}.

2.6.3. *Particle size and particle size distribution*

Particle sizes and particle size distribution of the polymerized nano emulsion binder were determined using a JEOL-2100 HR, transmission electron microscope and particle size distribution was determined using Leica Qwin 500 image analyzer

2.6.4. *Molecular Weight determination*

The polymerized nano-emulsion latex molecular weight was recorded by using Styrogel HR-DMF, (3µm), 7.8 × 300 mm, Water Comp. Ireland, (5000-600000) one column. The 0.01 g sample was dissolved in 2 ml of solvent, and then it filtrated by siring filter (0.45 µ).Then the sample introduces in GPC device.

2.6.5. *Rheological measurement*

Rheological properties of nano latex were studied using Brookfield Digital Rheometer; model HA DVIII Ultra (Brookfield Engineering Laboratories INC.), with spindle no. SC4-21. The rheological parameters for prepared nano binders were measured at room temperature.

2.7. Evaluation of printed fabric

2.7.1. *Color measurements*

The color strength of the printed specimens was assessed by reflectance method, (Abo-Shosha et al., 2009) which performed on PERKIN – ELMER Lambda 3B, UV/V Spectrophotometer. The color strength expressed as K/S was evaluated by applying the Kubelka Munk equation (Kubelka & Munk, 1931; Mehta, Bhavsar, Vora, & Shah, 1984) as follows:

$$K/S = \frac{(1-R)^2}{2\mathrm{R}} - \frac{(1-R_0)^2}{2\mathrm{R}_0}$$

Where: R, R_o are decimal fractions of the reflectance of the printed and unprinted fabric, respectively. K = absorption coefficient. S = scattering coefficient.

2.7.2 *Stiffness properties*

Printed and unprinted samples Stiffness was measured by using ASTM test method D 1388 – 96 using the cantilever apparatus (ASTM 1388 – 96, 2002). (ASTM Standard Test Method C33 (ASTM D–1388–08), 2012)

2.7.2. *Fastness properties*

Washing, rubbing and perspiration fastness was evaluated by using the standard method. (AATCC, 1993a, 1993c, 1993d) Light fastness was assessed according to AATCC test method. (AATCC, 1993b) The gray scale reference was used to evaluate the color change. (AATCC_Technical_Manual, 2008)

J
T
A
T
M

3. Results and discussion

3.1. Characterization of prepared nano-emulsion

3.1.1. *Optimization of reaction conditions*

3.1.1.1. Effect of monomer concentration ratio

Our modified micro-emulsion polymerization process includes several steps: (1) small amount of monomer (2 ml) was added to initiate the polymerization reaction in an original micro-emulsion, (2) it is very important to add the most of the monomer (18 ml) slowly during this stage to prevent a development of unreacted monomer droplets; and (3) post addition reaction

In step (1), fixed polymerization recipes was done, including monomer concentration, while ACA/BMA ratio was varied. Table 1 indicates various monomer compositions, which used to prepare the nano-emulsions.

Table 1 provide that, the average particle size (nm) as well as molecular weight (g/mol.) of the prepared nano-emulsion increased gradually from 24.97 to 240 nm and from 1.1156 to 8.178 g/mol. respectively when using UM. While using TM provide slightly increased in the average particle size from 210 to 326.7 nm, but the molecular weight is very high, according to ACA/BMA ratio. However, as the ACA/BMA ratio increase the average particle size and molecular weight of the obtained nano-emulsion increased dramatically, in both methods. This is may be due to that, adding acrylic acid cause modify the surface of the nano emulsion particles, which led to increase the cross-linking and adhesion among nano emulsion particles (Zosel, Heckmann, Ley, & Mächtle, 1987).

From result listed in Table 1, it is notice that the particle size and molecular weight of the prepared nano-emulsion using TM method is higher than using UM method. This is attributed to that, the effect of ultrasonic sterile. This may due to the bubble formation and collapse which known as cavitation.

In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured (Kingery, Bowen, & Uhlmann, 2006). The temperature at which the amorphous phase of the polymer is changed between rubbery and glassy states is called glass transition temperature (Tg). Tg constitutes the most important mechanical property for all polymers. The Tg of the polymer that used in pigment printing binder can be varied from -24°C (soft) to +15°C (tough).

During the study it was found that, the Tg of different prepared nano-emulsion ranges from (-2.7 to +3.7) when using UM, while it ranged from (+5.7 to +1.4) when using TM. That indicates the glassy state of prepared nano-emulsion is typically formed by cooling to very low temperature and solidification from the molten (or liquid) state, so the printing pastes which contain the prepared binders by using two methods will keep its viscosity at different temperature, therefore it can be used it as binders for textile pigment printing.

J
T
A
T
M

Table 1. Effects of monomer concentration ratio on the properties of prepared nano emulsion

ACA/ BMA ratio	MW (g/mol.)		Particle size (nm)		(Tg°C)		Coagulation		Color	
	UM	TM	UM	TM	UM	TM	UM	TM	UM	TM
100/0	1.137	10.99	53.1	210	3.7	5.8	No	Some	Milky	Transparent
75/25	1.156	20.99	47.3	173	3.1	4.4	No	Some	Milky	Transparent
50/50	1.285	23.79	25.0	55	-1.89	3.9	No	Some	Milky	Milky
25/75	2.227	Very high	55.7	202	-1.17	1.8	No	Always	Milky	Milky
0/100	8.178	Very high	190	327	-2.7	-1.3	Some	Always	Milky	Milky

3.1.1.2. Effect of emulsifier concentration

Emulsifier content was changed from 2 to 6 g wt.%, while other experimental conditions was kept without changed in order to study its effect. Figure 1 showed that the average particle size of obtained nano emulsion is decreasing as increasing emulsifier concentration when we apply two methods. Also, it was observed that, at very low concentration of

SDS (2 g wt.%), a large particle size was obtained. It suggested that, low concentration of used emulsifier prevent the particles flocculating. Figure 1 proved that, the average particle size was smaller when apply UM compared to TM. This is attributed to the ultrasonic effect, which caused cavitation bubbles.

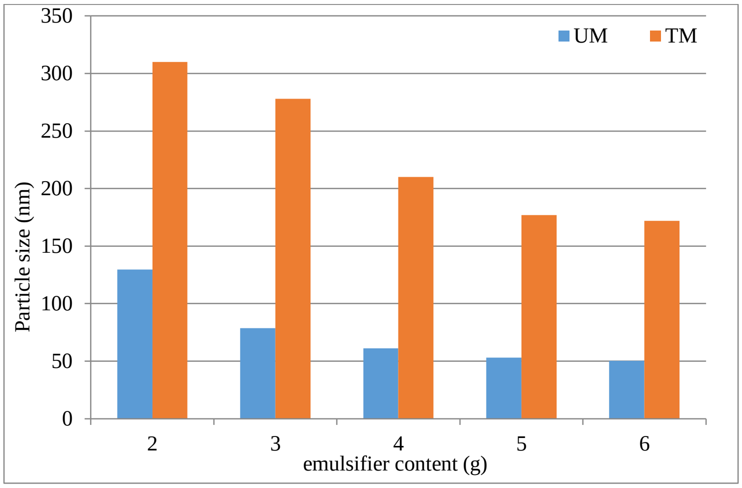


Figure 1. Effect of emulsifier content on particle size of prepared binder in both methods (traditional and ultrasonic)

JTATM

3.1.1.3. Effect of initiator content

During this step, the initiator concentration was changed from 0.1 to 0.5 g wt.%, while keeping other experimental conditions without changing. Fig.4 proven that, as KPS concentration increased the average particle size slightly increased until 0.3 g and 0.4 g wt.% when using UM and TM respectively, while, at 0.5 g wt.% KPS, the average particle size of the prepared nano emulsion was relatively large in both methods. This result may be due to using high initiator concentration which cause increasing in the nucleation activity (increasing the number of growing particles) which lead to the occurrence of inter particle aggregation.

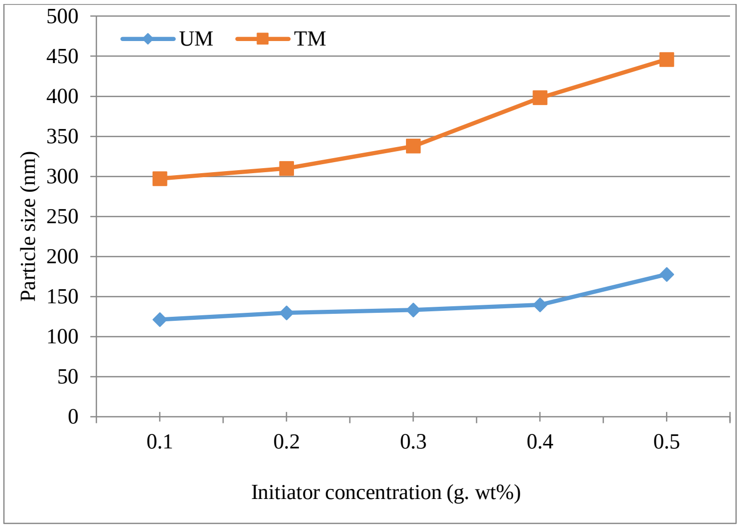


Figure 2. Effect of initiator concentration on particle size of prepared binder using both methods (traditional and ultrasonic)

3.1.1.4. Effect of total monomer content

Four experiments with total monomer content of 5, 10, 14 and 20 wt.%, respectively, were carried out to study the effect of the total monomer content on particle size of the obtained nano-emulsion, while keeping all polymerization recipes were fixed. From Figure 3 it is noticed that as the total monomer content increase the particle size of prepared nano-emulsion decrease until 14 wt%, after that, it increase dramatically when using UM method, while when using TM the particle size decrease as the total monomer content increase until 20wt%. This may be attributed to the ultrasonic wave effect.

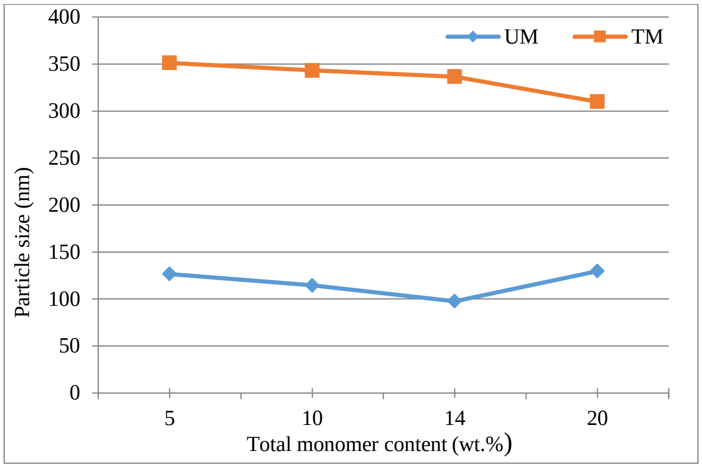
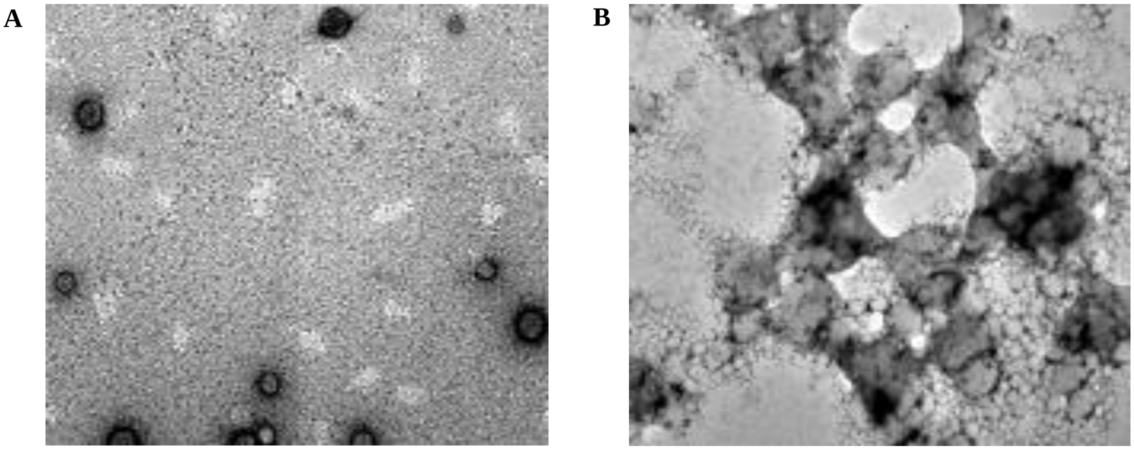


Figure 3. Effect of total monomer effect on particle size of prepared binder using both methods (traditional and ultrasonic)

JTATM

3.1.2. Morpholgical and Physical Properties

In addition, it is observed that, at low concentration of ACA (50/50 wt%) the prepared nano emulsion has homogeneous, compatible and stable (Figure 4), while at 100/0 wt.% ACA/BMA, the prepared nano-emulsion show large particle size (Figure 4) as well as high molecular weight. These result may arise from, at high concentration of ACA/BMA the inter particle aggregation will be takes place.



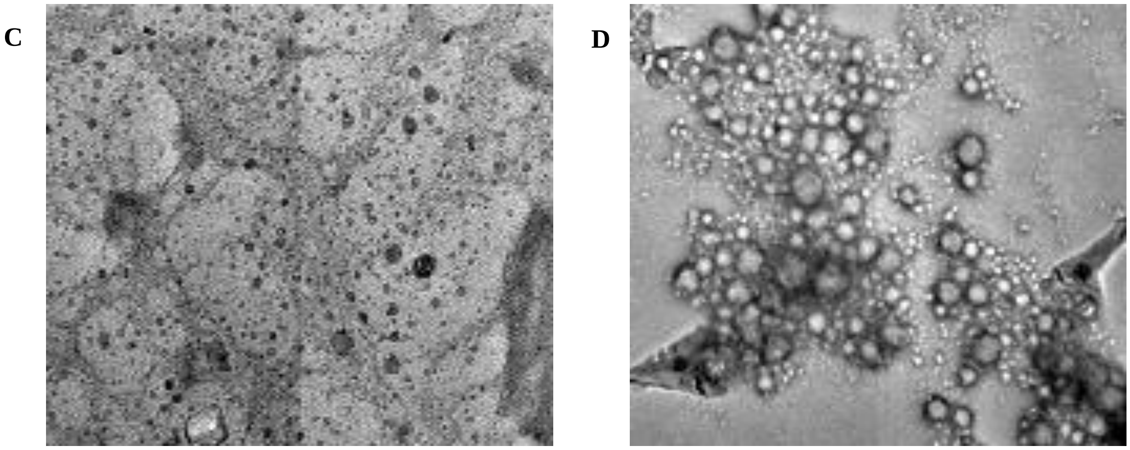


Figure 4: TEM images of prepared nano-emulsion using traditional (TM) and ultrasonic (UM) methods

a) TM 50/50 AAC/BMA b) TM 100/0 AAC/BMA
c) UM 50/50 AAC/BMA d) UM 100/0 AAC/BMA

3.1.3. FT-IR analysis

The acrylic and methacrylic ester are interesting chemicals with two reactive sites vinyl and ester groups but the reactions of vinyl groups are the more important. As a site for polymerization reaction, the vinyl groups lead to a wide variety of homo and copolymer with broad ranges of properties. The vinyl group can also undergo addition reaction with a variety of reagents and thus makes these ester valuable chemical intermediates for synthesis many useful compounds.

FT-IR spectrums of the prepared nano-emulsion under the optimum condition (50/50 wt.% ACA/BMA, 5 g wt.% SDS, 0.3 g wt.% KPS and 14% total monomer content), using UM, and TM are shown in Figure 5.

The absence of vinyl group absorption at 1636 cm^{-1} confirms the co-polymerization process takes place between ACA and BMA. The broad peak at 3438 cm^{-1} with correlation intensities of 88.950 was associated with the (-OH) of carboxylic group. The peak detected at 1715 cm^{-1} with correlation intensities 93.742 belongs to the extending vibration of carbonyl groups (C=O). The absorbance of stretching carboxylic group (=C-O) and that ester group (C-O) was detected at 1240 and 1160 cm^{-1} with correlation intensities 94.891 and 93.57 respectively. These results provide that the copolymerization process took place between ACA and BMA as shown in Figure 5 and the active carboxylic group remains unaffected during this process.

J
T
A
T
M

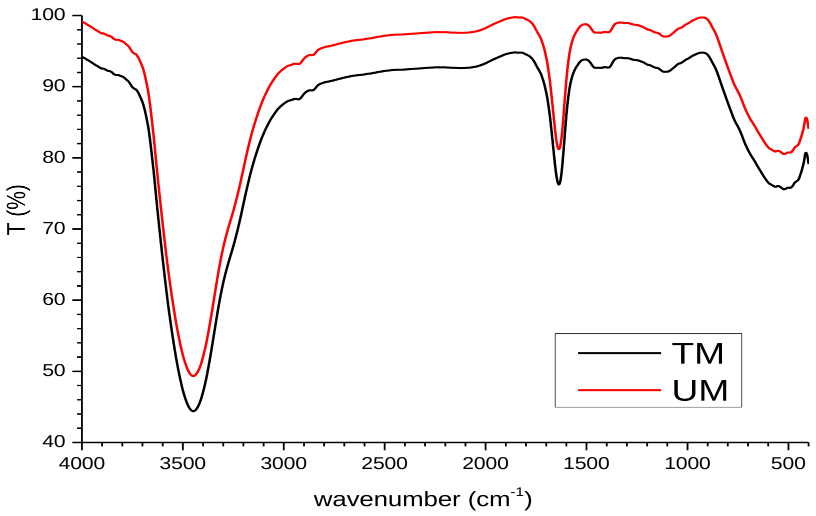


Figure 5. FT-IR spectra of prepared nano-emulsion using traditional and ultrasonic methods

3.1.4. Rheological Properties

It is very important to study the rehological properties for both prepared nano-emulsion, because the rheological properties are responsible for controlling dye penetration, depth of shade, sharpness of the print and levelness.

From Figure 6 it is clear that, both examined samples are characterized by non-Newtonian pseudo plastic behavior, where the up and down flow curves are coincident. It is also clear that the location of the rheogram and its slope seems to be dependent on the used method.

However, in the use of the binder with traditional method, the viscosity values are higher than ultrasonic method, which indicates an increase in its apparent viscosity. This may be attributed to the effect of ultrasonic irradiation on the prepared binder.

J
T
A
T
M

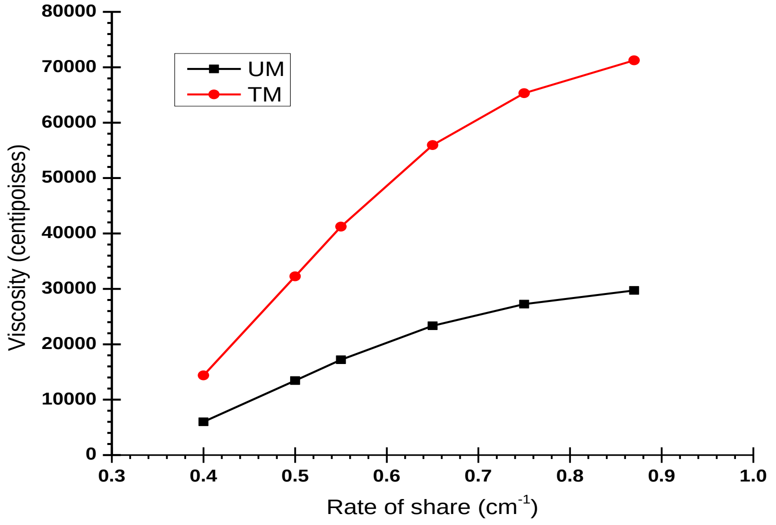


Figure 6. Rheological properties of prepared nano-emulsion using traditional and ultrasonic methods

Increasing the rate of share higher than 1 showing that, the apparent viscosity decreases as the rate of shear increases (prepared binders show shear thinning characteristics). The data obtained are given in

Table 2. It can be seen that the apparent viscosity values of the binder using ultrasonic method are lower than those of the binder using traditional method, which reduce the amount of the thickener used in the printing pastes.

Table 2. Apparent viscosity of prepared nano-emulsion using traditional and ultrasonic methods

Rate of shear (sec^{-1})	Viscosity (centipoises)		
	Ultrasonic method	Traditional method	
2.06	12000	60633	
2.33	10235	49511	
3.1	8937	44023	
3.71	7970	37233	
4.09	6991	33235	
4.53	7189	31253	

3.2. Effect of prepared nano-emulsion binder on properties of printing fabric

3.2.1. Effect of Curing Time and Curing Temperature on K/S Values

From fig. 9, it is obvious that when curing temperature increases the K/S also increases; and the optimum of fixation temperature is 130°C, 150°C for prepared binder by using SM and TM respectively. While from fig. 6 we noticed that when the curing time of the printed fabric with prepared binder increase, the K/S values decreased. The highest K/S values, 14.24, 10.34 have been recorded after 2 and 4 minutes for prepared binder by using UM and TM respectively.

J
T
A
T
M

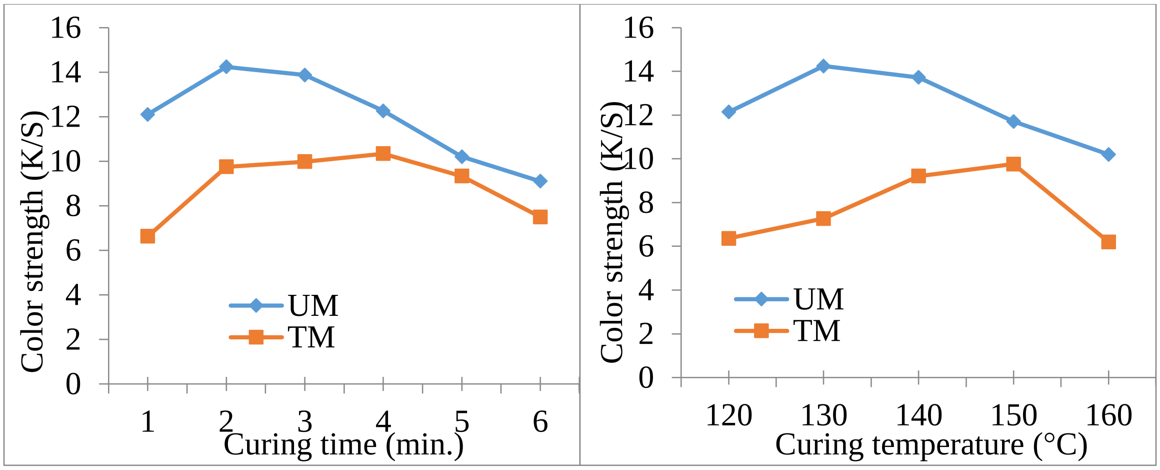


Figure 7. Effect of curing time and temperature on K/S of printed fabric Conditions: For curing time; curing temperature is 130°C for UM and 150°C for TM) for curing temperature, curing time is 2 min.

3.2.2. Effect of Binder content on color strength values (K/S)

Pigment particles are considered as molecular aggregates that does not contain any groups capable of interacting with fibers or substrate. Using pigment dyes is required a binder to help in attached to the fibers, which is a high molecular weight film forming material. The binder plays crucial part in determining the color strength of the finished fabric because it is the main linkage between pigment and the fibers. From the data in Figure 8, it is notice that as the binder content increases, the K/S values of printed samples are increases based on the binder used. However, the K/S values listed for fabric printed with binder prepared by UM were higher than the fabric printed with binder prepared by TM method (Figure 8). The highest values of K/S, 14.24, 8.74 achieved at a prepared binder concentration of 20, 25 g/l by using UM and TM respectively.

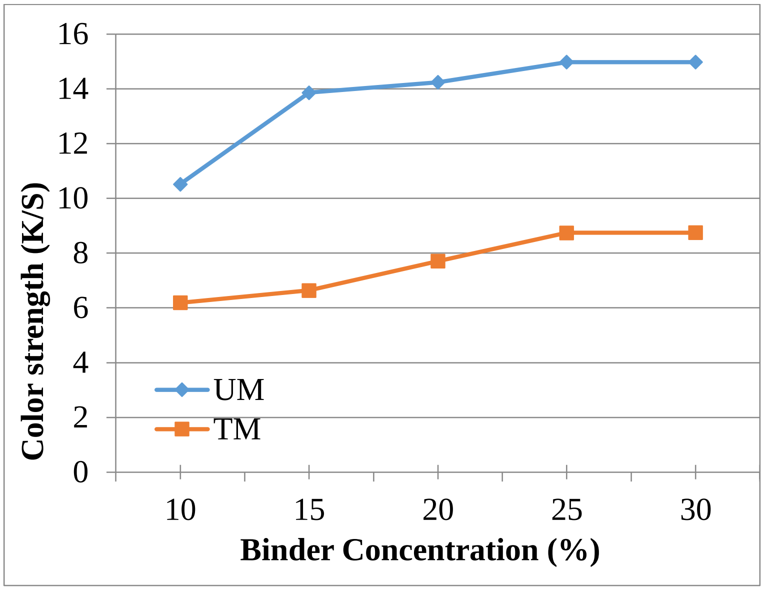


Figure 8. Effect of binder concentration in printing paste on the K/S values of printed cotton fabric

3.2.3. Effect of monomer concentration ratio on K/S and fastness properties

The data listed in Table 3 illustrate that, the color strength (K/S) as well as stiffness increased with the decrease of ACA/BMA ratio. Dry and wet rubbing fastness values are depending on ACA/BMA content and preparation method, it ranges from 3-4 when use UM while it ranging from 2-3 when use TM. Furthermore, it is notice that, all prints ranging from excellent to very good fastness to washing, and perspiration when using UM but ranging from poor to good when using TM method.

For light fastness, it clear that all prints ranging from very good to excellent. In addition, all samples have good handle, except the sample of 50/50 ACA/BMA shows slight increase in stiffness. This may be attributed to the reaction occurred between the active carboxylic group of BMA with the functional groups present on the fiber surface, causing strengthening the binder film, which lead to enhancing the adhesion between the binder film and the pigment, causing improve the fastness properties of the printing sample.

Table 3. Effects of ACA/BMA content ratio on the color strength, stiffness and fastness properties of the print sample

ACA/BMA Ratio	K/S	Stiffness	Washing fastness		Rubbing fastness		Perspiration fastness				Light fastness
							Acidic		Alkaline		
			Alt	St.	Wet	Dry	Alt.	St.	Alt.	St.	
Ultrasonic Method (UM)											
100/0	8.3	1.553	3-4	3-4	3-4	3	3-4	3-4	3-4	3	6-7
75/25	8.9	1.522	3-4	3-4	3-4	3	3-4	3	3	3	7
50/50	9.5	1.487	4	4	3-4	4	4	4	4	3-4	7
25/75	8.7	1.447	3-4	4	3-4	4	4	4	4	3-4	6-7
0/100	7.7	1.421	3	3	3	3	3	3	3	3	6-7
Traditional Method (TM)											
100/0	6.3	1.985	3	3	3	3-4	3	3	3	3	6
75/25	6.9	1.932	3	3	3	3-4	3	3	3	3	6
50/50	7.4	1.891	3-4	3-4	3	4	3	3	3	2-3	6-7
25/75	7.1	1.765	3	3	3	3	3	3	2-3	2-3	6
0/100	5.8	1.702	2-3	2-3	2-3	2	2-3	3	2-3	2-3	5-6

3.2.4. Effect of prepared binder on K/S and fastness properties of prints cotton fabric

Table **4** shows the fastness properties of printed cotton fabrics using the prepared binder under optimum conditions. From the data listed in Table 4, it is observed that, there are small differences in the fastness properties of the pigment printed samples of cotton fabrics. From these results, it is clear that, the fastness properties of printed fabric using prepared binder by UM ranging from very good to excellent for all fastness properties, while the printed fabric using prepared binder by TM is ranging between good to very good for washing, perspiration as well as light fastness, while from poor to good for crocking fastness.

JTATM

Table 4. K/S and fastness properties of printed sample using the both obtained binder with cotton fabrics

Heating method	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Light fastness
						Acidic		Alkaline		
		Alt	St.	Alt.	St.	Alt	St.	Alt	St.	
UM	10.2	3-4	4	4-5	4-5	4	3-4	4	4	7
TM	7.8	2-3	2-3	3	3-4	2-3	2-3	3	2-3	6-7

4. Conclusion

A nano-scale polymer micro-emulsion based on butyl methacrylate (BMA) with high monomer/surfactant ratio acrylic acid was successfully synthesized using Ultrasonic homogenizer. This Prepared nano latexes exhibited narrow particle size distribution with the particle diameter less than 50 nm and high stability with the help of the co-polymerizable surfactant, all of this rely upon monomer, initiator content, emulsifier concentration wt.% ratios in addition to total monomer content. The nano latexes prepared and pigment dispersions were applied in textile printing by using flat screen technique. The resulted fabrics printed by the above binder exhibited excellent fabric color fastness, good handle and high color yield.

5. Acknowledgement

It is our pleasure to give great thankful to soul of Dr. Zain Mohamed, who is one of co-authors of this article for his helping during working process, because he was died before publishing this article.

6. References

AATCC. (1993a). Colour Fastness to Crocking *Technical Manual Method* (Vol. 68, pp. 23-25): American Association of Textile Chemists and Colorists.

AATCC. (1993b). Colour Fastness to Light: Carbon – Arc Lamb, Continuous Light *Technical Manual Method* (Vol. 68, pp. 33-48): American Association of Textile Chemists and Colorists.

AATCC. (1993c). Colour Fastness to Perspiration *Technical Manual Method* (Vol. 68, pp. 30-32): American Association of Textile Chemists and Colorists.

AATCC. (1993d). Colour Fastness to Washing: Characterization of Textile Colorants *Technical Manual Method* (Vol. 68, pp. 89): American Association of Textile Chemists and Colorists.

AATCC_Technical_Manual. (2008). *AATCC_Technical_Manual* (Vol. 83). Research Triangle Park, NC 27709, USA: American Association of Textile Chemists and Colorists.

Abo-Shosha, M. H., Nassar, F. A., Haggag, K., El-Sayed, Z., & Hassabo, A. G. (2009). Utilization of Some Fatty Acid/PEG Condensates as Emulsifiers in Kerosene Paste Pigment Printing. *Research Journal of Textile and Apparel, 13*(1), 65-77.

Amigoni-Gerbier, S., Desert, S., Gulik-Kryswicki, T., & Larpent, C. (2002). Ultrafine Selective Metal-Complexing Nanoparticles: Synthesis by Microemulsion Copolymerization, Binding Capacity, and Ligand Accessibility. *Macromolecules, 35*(5), 1644-1650. doi: 10.1021/ma0113632

Amigoni-Gerbier, S., & Larpent, C. (1999). Synthesis and Properties of Selective Metal-Complexing Nanoparticles. *Macromolecules, 32*(26), 9071-9073. doi: 10.1021/ma991254b

ASTM Standard Test Method C33 (ASTM D–1388–08). (2012). Standard Test Methods for Stiffness of Fabrics. West Conshohocken, PA: ASTM International.

Chow, G.-M., & Gonsalves, K. E. (1996). *Nanotechnology: Molecularly Designed Materials* (Vol. 1st Edition). Washington, DC: American Chemical Society.

Davda, J., & Labhasetwar, V. (2002). Characterization of nanoparticle uptake by endothelial cells. *Int J Pharm, 233*(1-2), 51-59.

De, S., & Robinson, D. H. (2004). Particle size and temperature effect on the physical stability of PLGA nanospheres and microspheres containing Bodipy. *AAPS PharmSciTech, 5*(4), 18-24. doi: 10.1208/pt050453

El-Zawahry, M. M., Abdelghaffar, F., Abdelghaffar, R. A., & Hassabo, A. G. (2016). Equilibrium and kinetic models on the adsorption of Reactive Black 5 from aqueous solution using Eichhornia crassipes/chitosan composite. *Carbohydrate Polymers, 136*, 507-515. doi: http://dx.doi.org/10.1016/j.carbpol.2015.09.071

Haggag, K., Abd El-Ghaffar, M. A., Kantouch, F. A., Hashem, A. I., Ramadan, A. A., & Mahmoud, Z. M. (2012). Synthesis of Glycidyl Methacrylate-Acrylic acid Copolymer Via Modified Microemulsion Polymerization and Using It As Textile Pigment Printing Binder. *Journal of Applied Sciences Research, 8*(10), 5169 - 5176.

J T A T M

Harvey, G., Gachagan, A., & Mutasa, T. (2014). Review of high-power ultrasound-industrial applications and measurement methods. *IEEE Trans Ultrason Ferroelectr Freq Control, 61*(3), 481-495. doi: 10.1109/tuffc.2014.2932

Hassabo, A. G. (2011). *Synthesis and Deposition of Functional Nano-Materials on Natural Fibres* (PhD Degree Polymer Chemistry), RWTH Aachen University.

Hassabo, A. G. (2014). New approaches to improving thermal regulating property of cellulosic fabric. *Carbohydrate Polymers, 101*(0), 912-919.

Hassabo, A. G., Erberich, M., Popescu, C., & Keul, H. (2015). Functional polyethers for fixing pigments on cotton and wool fibres. *Research & Reviews in Polymer, 6*(3), 118-131.

Hassabo, A. G., Mendrek, A., Popescu, C., Keul, H., & Möller, M. (2014). Deposition of Functionalized Polyethylenimine-Dye onto Cotton and Wool Fibres. *Research Journal of Textile and Apparel, 18*(1), 36-49.

Hassabo, A. G., & Mohamed, A. L. (2016). Multiamine Modified Chitosan for Removal Metal Ions from their Aqueous Solution *BioTechnology: An Indian Journal, 12*(2), 59-69.

Hassabo, A. G., Nada, A. A., Mohamed, A. L., & Abou-Zeid, N. Y. (Accepted for publication 2015). Properties of Cellulosic Fabrics Treated by Water-repellent Emulsions. *Indian journal of fibre & textile research*.

Hassabo, A. G., Schachschal, S., Cheng, C., Pich, A., Popescu, C., & Möller, M. (2014). Poly (vinylcaprolactam)-based Microgels to Improve Gloss Properties of Different Natural Fibres. *Research Journal of Textile and Apparel, 18*(1), 50-63.

Ibrahim, N. A., El-Sayed, Z. M., Fahmy, H. M., Hassabo, A. G., & Abo-Shosha, M. H. (2013). Perfume Finishing of Cotton / Polyester Fabric Crosslinked With DMDHEU in Presence of Some Softeners. *Research Journal of Textile and Apparel, 17*(4), 58-63.

Jena, P., & Behera, S. N. (1996). *Clusters and Nanostructured Materials Hardcover*. New York, USA: Nova Science Pub. Inc.

Kingery, W. D., Bowen, H. K., & Uhlmann, D. R. (2006). *Introduction to Ceramics* (Vol. 2nd Edn.). New York: John Wiley & Sons.

Kubelka, P., & Munk, F. (1931). Ein Beitrag zur Optik der Farbanstriche. *Z. Tech. Phys., 12*, 593.

Kumer, J. M., Wolfbeis, O. S., & Klimant, I. (2002). Homogeneous luminescence decay time-based assay using energy transfer from nanospheres. *Anal Chem, 74*(9), 2151-2156.

Larpent, C. (2003). Microemulsion Polymerization: A Way to Synthesize Well-Defined Highly Functionalized Nanoparticles. In A.-h. El-Aissar (Ed.), *Colloidal polymers: Synthesis and Characterization* (Vol. 115, pp. 145 - 232). New York, USA: Marcel Dekker.

Lu, J., & Rosenzweig, Z. (2000). Nanoscale fluorescent sensors for intracellular analysis. *Fresenius' Journal of Analytical Chemistry, 366*(6-7), 569-575.

Mehta, K. T., Bhavsar, M. C., Vora, P. M., & Shah, H. S. (1984). Estimation of the Kubelka--Munk scattering coefficient from single particle scattering parameters. *Dyes and Pigments, 5*(5), 329-340.

Mohamed, A. L., El-Naggar, M. E., Shaheen, T. I., & Hassabo, A. G. (2016). Novel nano polymeric system containing biosynthesized core shell silver/silica nanoparticles for functionalization of cellulosic based material. *Microsystem Technologies, 22*(5), 979-992. doi: 10.1007/s00542-015-2776-0

J
T
A
T
M

Mohamed, A. L., El-Sheikh, M. A., & Waly, A. I. (2014). Enhancement of flame retardancy and water repellency properties of cotton fabrics using silanol based nano composites. *Carbohydrate Polymers, 102*, 727-737. doi: http://dx.doi.org/10.1016/j.carbpol.2013.10.097

Mohamed, A. L., Er-Rafik, M., & Moller, M. (2013a). Suitability of Confocal Raman microscopy for monitoring the penetration of PDMS compounds into cotton fibres. *Carbohydrate Polymers, 96*(1), 305-313. doi: http://dx.doi.org/10.1016/j.carbpol.2013.03.087

Mohamed, A. L., Er-Rafik, M., & Moller, M. (2013b). Supercritical Carbon Dioxide Assisted Silicon based Finishing of Cellulosic Fabric: A Novel Approach. *Carbohydrate Polymers, 98*(1), 1095–1107. doi: http://dx.doi.org/10.1016/j.carbpol.2013.06.027

Mohamed, A. L., & Hassabo, A. G. (2015). Flame Retardant of Cellulosic Materials and Their Composites. In P. M. Visakh & Y. Arao (Eds.), *Flame Retardants* (pp. 247-314): Springer International Publishing.

Moser, W. R. (1996). Advanced Catalysts and Nanostructured Materials, Modern Synthetic Methods. San Diego, CA: Academic Press.

Niemeyer, C. M. (2001). Nanoparticles, Proteins, and Nucleic Acids: Biotechnology Meets Materials Science. *Angewandte Chemie International Edition, 40*(22), 4128-4158. doi: 10.1002/1521-3773(20011119)40:22<4128::AID-ANIE4128>3.0.CO;2-S

Park, E. J., Brasuel, M., Behrend, C., Philbert, M. A., & Kopelman, R. (2003). Ratiometric optical PEBBLE nanosensors for real-time magnesium ion concentrations inside viable cells. *Anal Chem, 75*(15), 3784-3791.

Steele, R., & Schiwall, R. P. (1959). Density Changes in Cellulose Treated With Urea-Formaldehyde Resins. *Textile Research Journal, 29*(3), 228-234. doi: 10.1177/004051755902900306

Stupp, S. I., LeBonheur, V. V., Walker, K., Li, L. S., Huggins, K. E., Keser, M., & Amstutz, A. (1997). Supramolecular Materials: Self-Organized Nanostructures. *Science, 276*(5311), 384-389.

Sumner, J. P., Aylott, J. W., Monson, E., & Kopelman, R. (2002). A fluorescent PEBBLE nanosensor for intracellular free zinc. *Analyst, 127*(1), 11-16. doi: 10.1039/B108568A

Visakh, P., & Arao, Y. (2015). Flame Retardants: Polymer Blends, Composites and Nanocomposites: Springer.

Waly, A. I., Abou-Zeid, N. Y., Marie, M. M., El-Sheikh, M. A., & Mohamed, A. L. (2009). Special Finishing of Cotton to Impart Flame-Retardancy, Easy Care Finishing and Antimicrobial Properties. *Research Journal of Textile and Apparel, 13*(3), 10-26.

Waly, A. I., Marie, M. M., Abou-Zeid, N. Y., El-Sheikh, M. A., & Mohamed, A. L. (2012). Processes of Dyeing, Finishing and Flame Retardancy of Cellulosic Textiles in the Presence of Reactive Tertiary Amines. *Research Journal of Textile and Apparel, 16*(3), 66 - 84.

Zosel, A., Heckmann, W., Ley, G., & Mächtle, W. (1987). Chemical heterogeneity in emulsion copolymers of carboxylic monomers. *Colloid and Polymer Science, 265*(2), 113-125. doi: 10.1007/BF01412754

J T A T M