Sigma J Eng Nat Sci, Vol. 41, No. 5, pp. 1029–1041, October, 2023

Sigma Journal of Engineering and Natural Sciences
Web page info: https://sigma.yildiz.edu.tr
DOI: 10.14744/sigma.2022.00049

Research Article

Influence of silica nanoparticles on the stability of paraffin wax emulsion

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ARTICLE INFO

Article history
Received: 08 October 2021
Revised: 14 November 2021
Accepted: 18 December 2021

Keywords:
Paraffin Wax Emulsion; Emulsifiers; Hydrophobicity; PEG-7 Glyceryl Cocoate; Silica Nanoparticles; Contact Angle; Emulsion Stability

ABSTRACT

Paraffin wax emulsions have been used widely in various areas. However, the basic problem faced in all areas is instability of emulsion. Different methods and emulsifiers have been proposed to overcome this problem. This study focuses on using a commercial emulsifier, (IK-8000) and aqueous silica nanoparticles to formulate paraffin wax emulsions and investigate their effects on the stability and mean diameter of paraffin wax emulsions. For comparison purpose, different emulsifier, PEG-7 Glyceryl Cocoate was used to stabilize one of 20 % (wt./wt.) paraffin wax emulsions. The PEG-7-Glyceryl Cocoate stabilized emulsion phase-separated after 3 days while the IK-8000 stabilized remained stable for more than a month. The effect of the silica nanoparticles on the emulsion's stability was studied by observing samples stored for over 2 months. It was seen that aqueous silica nanoparticles helped to increase the stability of the paraffin wax emulsions. Emulsions prepared without silica nanoparticles (only IK-8000) were stable for just a month (1 month) whereas those which were formulated with silica nanoparticles and IK-8000 remained stable for more than 2 months (> 2 months). However, the addition of aqueous silica nanoparticles did not have a significant effect on the mean particle size of the emulsion. It was observed that the addition of 0.5 mL aqueous silica nanoparticles to the paraffin wax emulsion first increased the mean particle size from 1.142 μm to 2.680 μm. Nonetheless, further increasing the amount of the aqueous silica nanoparticles from 1.0-5.0 mL decreased the mean particles size of the paraffin wax emulsion from 2.680 μm to 0.942 μm. The contact angle formed by water drop on the surfaces coated with different emulsion samples of 30%wt. PWE, 40%wt. PWE, 50%wt. PWE and 60 %wt. PWE were measured. The higher the degree of solid content in emulsion, the greater the contact angle measured thus higher hydrophobicity.

Cite this article as: İbrahim AP, Erdem İ, Gönen M. Influence of silica nanoparticles on the stability of paraffin wax emulsion. Sigma J Eng Nat Sci 2023;41(5):1029–1041.

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This paper was recommended for publication in revised form by Regional Editor Ali Erdoğmuş

Published by Yıldız Technical University Press, İstanbul, Turkey

INTRODUCTION

Paraffin wax emulsions have gained enormous attention from researchers for the last few decades due to their numerous applications (textile, forest products, fruits coating, ink, etc.). However, the main problem faced by researchers in this area is emulsion instability and its causes. An emulsion is defined as a heterogeneous system of two or more immiscible liquid phases (e.g., oil and water) [1]. One of the phases called as a dispersed phase is disseminated homogeneously in a dispersion medium named as a continuous phase [2] with the help of mechanical force (homogenizers) and surfactants [3]. Due to the immiscibility of the phases, emulsions are usually thermodynamically unstable but kinetically stable [4, 5, 6]. Basically, there are two type of emulsions depending on which phase is dispersed in the other (continuous phase). These are oil-in-water (O/W) and water-in-oil (W/O) emulsions [1]. Emulsions are classified into two groups based on the number of phases they are composed of. They are simple (two-phase) and multiple (three-phase) emulsions. Although it is very difficult to produce and stabilize multiple phase emulsion, they have many applications in various sectors like; pharmacy (drug delivery), cosmetics (hand creams) and food (mayonnaise, ice creams) [7]. According to IUPAC, emulsions consisting of water, oil and surfactant have a particle diameter of approximately 1-100 nm and are thermodynamically stable and known as nano-emulsions. Nano-emulsions are very similar to microemulsions. However, unlike self-forming micro emulsion, a mechanical force is applied to produce nano-emulsion for disrupting the dispersed phase further into nano scale [3].

Paraffin wax is a white solid obtained from petroleum or coal [8]. It consists of a uniform mixture of hydrocarbon molecules which usually contain about 20 to 40 carbon atoms. It can be distinguished as solid at ambient temperature (25 °C) and high viscosity in molten state (< 99 °C) [9, 10]. Paraffin wax is widely used in leather, paper, textile, forest and cosmetic products because of its high hydrophobic properties [9].

Silica is the main component of quartz and sand. It is also found in large quantities in biominerals that make up the skeletal structure of grasses and diatoms [11]. Silica, a naturally occurring mineral, is 99.5% SiO_2 and the remainder is inert components. As filler, it is available in three different forms: quartz (crystalline silica), vitreous silica and diatomaceous silica [12]. Generally, most of the silica used is produced by the wet methods such as; drying of sodium silicate, hydrolysis of alkoxysilane, acidic reaction of calcium silicate and by the dry methods like high temperature hydrolysis of silicone halide e.g. $SiCl_4$. Siloxane (≡Si-O-Si≡) and four groups of silanol (≡Si-OH) are present on the silica surface, and the physical properties of the silica surface change depending on the type of these groups. Surface modification of silica is performed by reacting silanol groups on the silica surface with alkoxysilane, silazane and/or siloxane to control the hydrophilic/hydrophobic property of the silica [11].

Surfactants, or emulsifiers, are amphiphilic molecules with a hydrophobic (lipophilic) tail consisting of a linear or branched polymeric chain and an ionic/non-ionic hydrophilic (lipophobic) head [13]. In addition, they can be obtained naturally or be synthesized [14]. Emulsifiers exhibit two main activities in the stabilization process. These are; providing colloidal stability to the dispersed particles by forming an electrically charged layer at the interface with the continuous phase and the other is reducing the surface tension between the two phases [15, 16]. The stability of an emulsion is described as its ability to maintain constant behavior of its basic parameters; density between the two phases, the dispersity and the uniform distribution of the dispersed phase in the medium over time [6, 17]. There are four main types of instability in emulsion. These are; flocculation/coagulation, coalescence/aggregation, cream formation/sedimentation and Ostwald ripening. Flocculation (coagulation) is the process where emulsion droplets/particles attract each other and form flocs without the rupture of the stabilizing layer at the interface. The same process occurs during coalescence (aggregation) of emulsion droplets. However, in coalescence, the layer at the interface is disrupted and the droplets form a single bigger drop [18]. This process happens when the repulsive force repelling the droplets further apart is lesser than the Van der Waals force attracting the droplets together [6]. Creaming or sedimentation occurs due to the effects of gravitational/centrifugal force. When either of these forces exceeds the Brownian motion of the dispersed droplets, a concentration gradient is induced in the emulsion such that larger mass of droplets that either sediment or floats depending on its density compared to the density of the continuous phase are formed [19]. In all cases, with time, there is a phase separation in the emulsion and this is called emulsion instability. Ostwald ripening is also another instability problem that mostly occurs in nano-emulsions. It takes place due to differences in chemical potential between droplets of various sizes. Ostwald ripening occurs in systems where the two phases have a non-negligible mutual solubility and the droplets are poly-dispersed. Small droplets have a greater solubility than large droplets due to the effect of curvature on surface free energy. Dispersed phase molecules diffuse from the surface of smaller droplets into the continuous phase and subsequently join up with larger droplets. As a result, small droplets become smaller and large droplets become larger leading to increment in mean droplet size [20].

A considerable number of investigations have been carried out on paraffin wax emulsion over the last few decades. Most studies focus on using various preparation methods and emulsifiers to enhance the stability as well as to manage the droplet size. In 2010, paraffin wax-in-water submicron emulsion (700 nm) was prepared by using low-energy emulsion inversion point (EIP) method. The effects of hydrophilic-lipophilic balance (HLB) value, surfactant

concentration, temperature and emulsification method on the emulsion stability & particle size was investigated. The emulsion was stabilized by Span 80/Tween 80. It was reported that a stable emulsion was obtained when the HLB value of the emulsifiers was between 9.5 and 10.3 [2]. In 2015, a study was conducted by using modified sodium dodecyl sulfate (SDS) as an emulsifier and ultrasonic homogenizer to prepare paraffin wax-in-water nano-emulsion. The effects of ultrasonic parameters (ultrasonic power & sonication time) and formulation-related parameters (emulsifier concentration) on the emulsion stability & particle size was examined. It was found that stable emulsion with droplet size about 160.9 nm could be obtained with the surfactant concentration of 10 mg/mL and treated at 40% of applied power (power density: 0.61 W/mL) for 15 min. It was reported that the emulsion prepared via ultrasonic cavitation was stable for more than 3 months [21]. In a recent study, a Pickering emulsion method was applied to produce particles that have two or more distinct properties on a single particle (i.e. Janus particles). Paraffin wax and silica nanoparticles (650 nm), cationic surfactants; hexadecyl-trimethylammonium bromide (CTAB) and didodecyldimethylammonium bromide (DDAB), polymeric surfactants; polyoxyethylene (20) cetyl ether (Brij 58) and polyoxyalkyleneamine (Zephrym PD7000) were used. The effects of the different surfactants on the stability of the Janus particles were investigated. It was observed that cationic surfactants produced the stable Janus particles at specific concentration [22]. Generally, the most studies aimed to improve the stability of paraffin emulsion since it is the main problem in industry. Span/80 and Tween 80 have been used more than any other emulsifier in the paraffin wax emulsions researches.

In the current study, the effect of silica nanoparticles on the stability of paraffin wax emulsions has been investigated. Previous studies where silica nanoparticles have been used to stabilize emulsions, oil was applied as the dispersed phase. Except for the studies where Janus particles was produced using Pickering emulsion method, no research has been conducted on emulsions where paraffin wax, emulsifier and silica nanoparticles were used by applying phase inversion method. The aim of this study is to investigate the effects of silica nanoparticles on the stability and mean diameter of paraffin wax emulsions which are used to provide hydrophobic properties to forest products e.g. (MDF, Chipboards, HDF etc.).

MATERIALS

Paraffin wax with melting point between (52-54°C) was obtained from Mercan Kimya, Denizli, Turkey. A commercial emulsifier (IK-8000) from Işıksan Kimya, İzmir, Turkey; PEG-7-Glyceryl Cocoate emulsifier (HLB=10) were acquired from Ataman Kimya, İstanbul, Turkey. Silica nanoparticles (15-35 nm) were purchased from Nanografi Nanotechnology, Ankara, Turkey. A distilled-water was produced in the laboratory of Chemical Engineering Department of Süleyman Demirel University.

METHODS

Water-Dispersed Silica Nanoparticles

Silica nanoparticles (15-35 nm) were dispersed in distilled water at a ratio of 1:100 (wt./v). After adding 1 g of silica nanoparticles to 100 mL of distilled water, the silica-water mixture was placed in an ultrasonic water bath (Jeio Tech, UCP-10) and sonicated for 15 minutes. The water-silica nanoparticles mixture was removed at the end of 15 minutes, and was stored for use in the emulsion's formulation. The silica concentration in this mixture is 1 % and will be referred to as aqueous silica nanoparticles throughout this study.

Paraffin Wax Emulsion Preparation

The Phase Inversion Method (PIM) was applied to produce the emulsions throughout this investigation. For the 20 % paraffin wax emulsion experiment; 79 % distilled water, 17 % paraffin wax and 3 % IK-8000 emulsifier were used. Based on the PIM method; the emulsifier (IK-8000) and paraffin wax were weighed separately and transferred into a 250 mL beaker and placed on a magnetic stirrer with heater. The temperature of this mixture was heated up to 70 °C, then, distilled water at the same temperature (70 °C) was added dropwise into the stirred mixture. After adding the required amount of water, 1 mL of the previously prepared aqueous silica nanoparticles was added to the emulsion obtained and the rapid stirring at 11,000 rpm proceeded until the mixture was finely homogenized. At the end of the process, the temperature of the emulsion was quickly reduced to ambient temperature in order to solidify the dispersed paraffin droplets into fine particles. The final emulsions obtained were stored for characterization [23]. All characterization procedures were performed at room temperature. The amount of aqueous silica nanoparticles was varied to examine its effect on the mean diameter and the stability of the emulsions. It should be noted that no aqueous silica nanoparticles were applied in the controlled experiments. A summary of the emulsion preparation has been given in the Figure 1 below.

20 %, 30 %, 40 %, 50 % and 60 % paraffin wax emulsions by weight were successfully prepared and the experimental details have been given in the Table 1 below.

Effect of Silica Nanoparticles on the Stability of Paraffin Wax Emulsion

In order to determine the effect of silica nanoparticles on the paraffin wax emulsion's stability, the aqueous silica nanoparticles were added in different amounts (0.5, 1.0, 3.0, 5.0 and 10.0 mL) to the emulsions during formulation. Six samples; API 7 (with only IK-8000), API 8 (with IK-8000 and 0.5 mL of aqueous silica nanoparticles), API 9 (with IK-8000 and 1.0 mL of aqueous silica nanoparticles), API

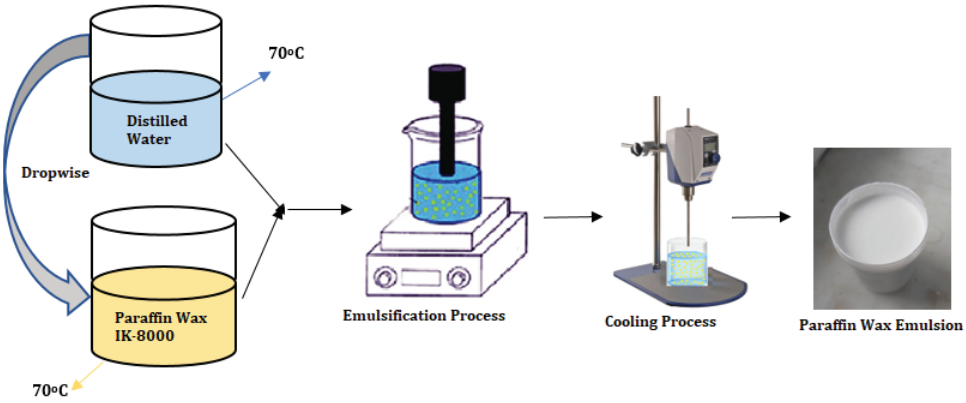


Figure 1. Flow Sheet of Paraffin Wax Emulsion Preparation.

Table 1. The Summary of the Constant and Variable Parameters

Emulsifier Type	Emulsifier Amount (%, wt)	Paraffin Wax (%, wt)	Additive (H_2O-SiO_2) (mL)	Temperature (°C)
IK-8000 *	3.0	17.0	0	70
IK-8000 +	3.0	17.0	0.5	70
Silica nanoparticles			1.0	
			3.0	
			5.0	
			10.0	
IK-8000 *	5.0	25.0	0	70
IK-8000 + Silica nanoparticles	5.0	25.0	0	70
IK-8000*	6.0	34.0	0	70
PEG-7-Glyceryl Cocoate	6.0	34.0	0	70
IK-8000 + Silica nanoparticles	6.0	34.0	0	70
IK-8000 *	7.0	43.0	0	70
IK-8000 + Silica nanoparticles	7.0	43.0	0	70
IK-8000 *	8.0	52.0	0	70
IK-8000 + Silica nanoparticles	8.0	52.0	0	70

* Were used as control experiment during the investigation of the effect of silica nanoparticles on the emulsion's stability.

10 (with IK-8000 and 3.0 mL of aqueous silica nanoparticles), API 11 (with IK-8000 and 5 mL of aqueous silica nanoparticles) and API 12 (with IK-8000 and 10 mL of aqueous silica nanoparticles) were prepared. The paraffin wax and IK-8000 contents were kept constant at 20 %,wt. and 3 %, wt. respectively in this study. The emulsification process was not different from the emulsion preparation method mentioned above in details. Samples of each emulsion from this experiment were kept for stability analysis over two months.

Influence of Silica nanoparticles on the Mean Diameter of the Paraffin Wax Emulsion

20 % (wt./wt.) paraffin wax emulsions containing 1.0, 3.0 and 5.0 mL of aqueous silica nanoparticles were prepared. The effect of the aqueous silica nanoparticles on the mean particle size was investigated by using dynamic laser light scattering (DLS) equipment (Nano ZS, Malvern Co., UK) to measure the mean diameter of the various emulsion samples. The results were compared to the mean particle size of the control sample (20 % PWE), which was prepared under the same experimental conditions explained in emulsion preparation section.

Contact Angle Measurements

Glass samples coated by using paraffin wax emulsions were used to measure the contact angles. A total of 5 samples were made available for this experiment. Samples were labeled as follows; Paraffin Wax (PW), 30 % Paraffin Wax Emulsion (30 % PWE), 40 % Paraffin Wax Emulsion (40

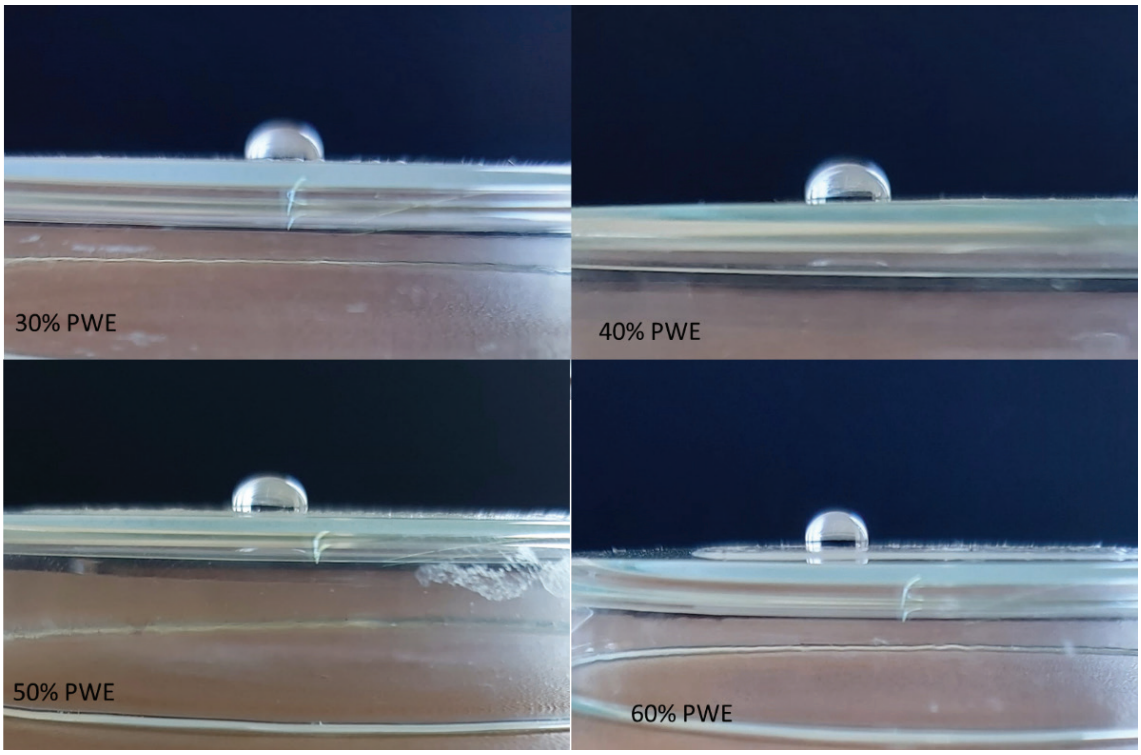


Figure 2. Images displaying water drops on glass surfaces coated by a different paraffin emulsion.

% PWE), 50 % Paraffin Wax Emulsion (50 % PWE) and 60 % Paraffin Wax Emulsion (60 % PWE). Thin film layers from each sample were formed on a flat glass surface. The film layers were left to dry, thus, the water phase evaporated leaving the paraffin wax phase behind. With the help of an automatic pipette, 10 microliters (10 μL) of water was dropped on paraffin coated glass surface. As shown below (Figure 2), clear images of samples were taken and the contact angle of each was measured using the Image J Application (1.45 bundled with 32-bit Java 1.6.0_20).

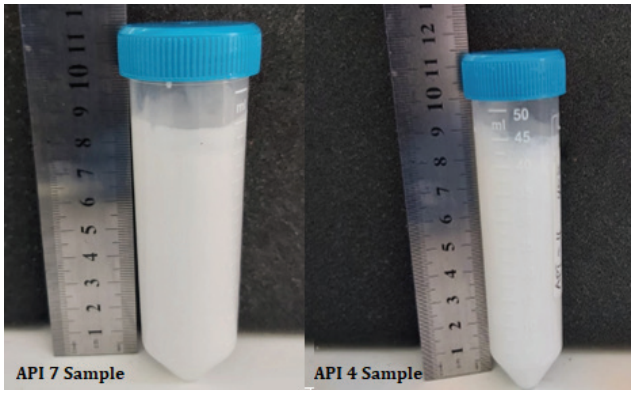


Figure 3. Initial state images of paraffin emulsions prepared using PEG-7-Glyceryl Cocoate (API 7) and IK-8000 (API 4).

Different Emulsifier's effect on the Stability of the Paraffin Wax Emulsion

PEG-7-Glyceryl Cocoate and a commercial emulsifier (IK-8000), were used to investigate the effects of different surfactant on the stability of the paraffin wax emulsion. These two emulsifiers were applied separately to stabilize 40 % (wt./wt.) paraffin wax emulsion. The emulsification process has been explained above in details. Both emulsions were stored under the same condition to observe their stability over time. Initial state images of the emulsions stabilized separately with both PEG-7-Glyceryl Cocoate and IK-8000 have been provided in Figure 3.

CHARACTERIZATION OF PARAFFIN WAX EMULSIONS

Emulsion's Stability Analysis

The emulsion's stability was determined by measuring the degree of gravitational phase separation in samples over time. Creaming and sedimentation values were determined from the ratio of the height of cream/sediment formed to the total height of emulsion samples in the tubes. For this experiment, 40 mL from each of the freshly prepared emulsions were transferred into 50 mL plastic tubes, capped and then stored for more than 2 months at room temperature (25°C). The emulsion's stability was monitored by visual observation, and the heights of the layer formed at the top and bottom of tubes were frequently measured. Emulsion's

stability (ES) was calculated as percentage of the total emulsion height (TEH) minus height of creamed layer (HCL) divided by total emulsion height (TEH):

$$ES\ (\%) = (TEH - HCL)/\ TEH \times 100 \quad (1)$$

Mean Diameter Analysis (MDA)

Mean diameter analysis of the emulsions was performed using dynamic laser light scattering (DLS) technique (Nano ZS, Malvern Instruments Co., UK). The instrument optimizes the depth and number of readings for every measurement by considering the concentration/opacity of the sample. The intensity of the scattered laser light was determined and the hydraulic mean diameter was calculated via Stokes-Einstein equation. The parameters defining the sample (viscosity, refractive index, etc. for both phases) were defined on the software of the instrument carefully to assure the correctness of the measurements. Samples were sonicated for 3 min before the measurements to remove the effect of viscosity and assure homogeneity. The loading of the samples to the square disposable polystyrene cuvette (DTS0012) was done using 3 mL plastic Pasteur pipettes carefully in order to prevent the formation of air bubbles. The measurements were performed at least 3 times without any dilution and the average values were reported in "μm".

RESULTS AND DISCUSSION

Effect of Silica nanoparticles on the Stability of the Paraffin Wax Emulsion

There are two means by which stabilizing agents keep an emulsion stable for longer period. One is the provision of stability by forming electrically charged layer/steric effect around the dispersed phase and the other is by reducing the interfacial tension between the two immiscible phases to allow them to be miscible. In either case, stable emulsions are formed for a specific time. Applying aqueous silica nanoparticles to the emulsions influenced its stability positively. Samples from freshly prepared emulsions stabilized with IK-8000+aqueous silica nanoparticles and only IK-8000 were stored and monitored for phase separation over time. It was observed that all samples were stable for the first month, thus, no trace of any form of instability was witnessed. However, after two months, a hint of phase separation was observed in the sample coded as API-7, which was prepared with only IK-8000 emulsifier. There were no signs of any sort of phase separation in samples; API-8, API-9, API-10, API-11 and API-12, which were prepared with IK-8000+aqueous silica nanoparticles. This can be related to the reason that IK-8000 emulsifier is a non-ionic emulsifier which only stabilizes the emulsion by reducing the interfacial force between the phases. Also, it may possess long chained monomers that can form steric effect around the dispersed nanoparticles to prevent them from flocculating. On the other hand, the stability in samples; API-8, API-9, API-10, API-11 and API-12 can be related to the aqueous silica nanoparticles which provide extra advantage in stabilizing the emulsion. The silica nanoparticles are adsorbed at the water-paraffin wax interface thereby strengthening the interfacial layer available. The increment of the interfacial contact area enables the formation of layers which are stable to droplets coalescence (Binks & Whitby, 2005). Moreover, silica nanoparticles have negatively charged surfaces due to the silozane and silanol groups present. The negatively charged silica nanoparticles may create repulsive forces that repel the dispersed phases. When the repulsive force exceeds the Van der Waal's force of attraction between the dispersed paraffin particles, they stay apart from each other thereby keeping the emulsion stable over time. The summary of the stability measurement was given in Table 2.

Influence of Silica nanoparticles on the Mean Diameter of the Emulsions

Four samples of 20%wt. PWE with various amounts of aqueous silica nanoparticles (0, 1.0, 3.0 and 5.0, mL), coded as API-20, API-21, API-22 and API-23, respectively) were characterized by measuring their mean diameters. According to the results, keeping the amount of the IK-8000 emulsifier constant (3 %) and increasing the quantity of aqueous silica nanoparticles initially increased the mean particle size then decreased it as given in Figure 5 (a). These results correspond to the ones reported in a study where both emulsifier and solid nanoparticles were applied to stabilize paraffin emulsion [24]. However, instead of the

Table 2. Stability analysis results of paraffin wax emulsions

Sample	1 min	5 min	15 min	1 hr	1 day	8 day	15 day	23 day	1 month	2 months
API-7	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*PS*
API-8	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*
API-9	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*
API-10	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*
API-11	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*
API-12	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*	*FE*

FE: Full emulsion, PE: Phase separation.

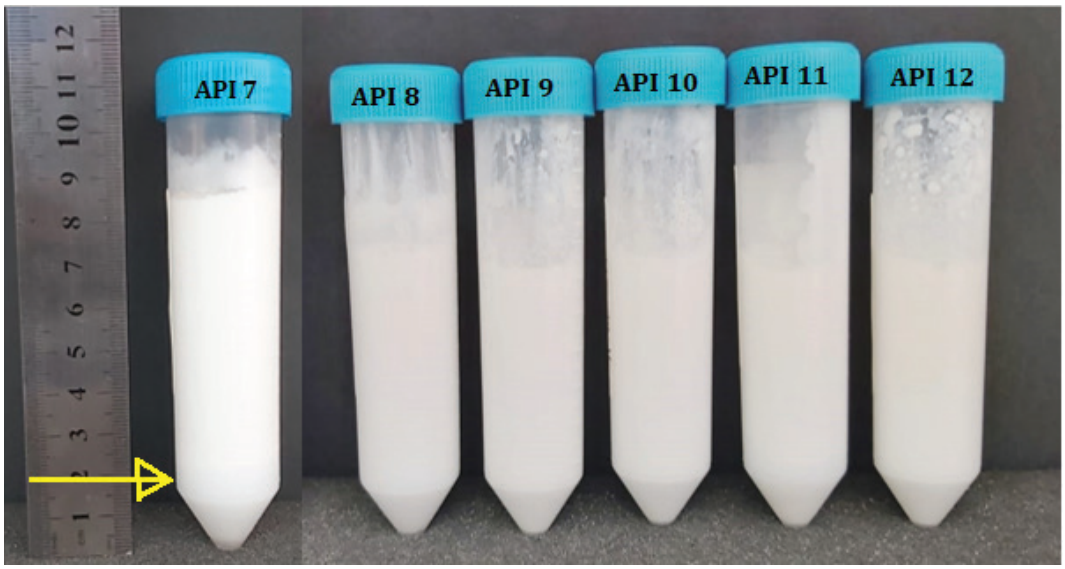


Figure 4. Images of samples API-7, API-8, API-9, API-10, API-11 and API-12 after two months of stability analysis.

mean diameter decreasing as the number of aqueous silica nanoparticles raises, the mean particle diameter increased initially then was reduced in the present study. Generally, silica nanoparticles have negatively charged surfaces due to the presence of siloxane and silanol groups on their surfaces [25]. The addition of a 1.0 mL of silica nanoparticles to the emulsion, those silica particles were adsorbed on the surface micelles thereby causing an increase in the mean particle size of the emulsion. However, that further addition of silica aqueous sol decreased the mean particle size of paraffin emulsion could not be explained in details. Thus further research needs to be performed for this issue. The prepared emulsion is a polydisperse one composed of droplets with varying mean diameter. The particle size distribution (PSD) was also analyzed via dynamic laser light scattering (DLS) equipment and the results are shown in Figure 5 (b). The particles were determined to be in the size range of 20-900 nm (volume-based distribution) for samples with varying aqueous silica content. The possible reason of having relatively higher mean droplet diameters may be related to the presence of larger droplets in relatively lower quantities which were not determined in PSD graphs. Although the PSD analysis was not accurate because of the polydispersity nature of the samples, it gave some clues about the size distribution of the droplets in the emulsions. The polydisperse emulsions prepared consist of 3 groups of dispersed particles: the particles within the size range of 20 to 100 nm, the particles within the size range of 200 to 900 nm and bigger particles in relatively lower ratio. The introduction of aqueous silica nanoparticles to the emulsions affected the PSD and the size ranges of the different groups of dispersed particles. Lower quantity of silica nanoparticles increased the ratio of smaller to larger particles resulting in a particle size range from 100 to 400 nm (which is seen as combined peaks for sample API-21). Increasing the silica content decreased the mean particle size which may be attributed to the reformation of the larger group of dispersed paraffin particles into smaller group ranging from 20 to 100 nm. However, the ratio of the smaller to larger group decreased with further increasing the silica nanoparticles content, thus, causing a decrease in the mean droplet size (Figure 5(a)). In the present study, DLS analyses were performed without diluting the samples unlike in some previous studies [24] and [26], where samples were diluted 500 and 1000 times, respectively. The polydispersity nature of the emulsions may be caused by the relatively high content of the paraffin phase dispersed. Koroleva *et al.,* 2017 [24] mentioned that the mean particle size increased significantly after increasing the paraffin wax fraction in the emulsion over 0.1. It was explained that increasing the paraffin wax content caused an increment in the emulsion viscosity making the homogenization harder to get nano droplets. The mean particle sizes reported by Koroleva *et al.,* 2017 were > 1000 nm for a paraffin fraction of ~16%wt. and > 5500 nm for a paraffin concentration of ~20%wt. prepared at 75°C (with 1%wt. Eumulgin O10 (nonionic surfactant) and 0.5%wt. PVA (for possible steric stability). The mean diameters for paraffin particles reported in the present work are smaller than those values reported by Koroleva et al. probably due to presence of IK-8000 emulsifier (in relatively higher amount, 3 %). Moreover, another reason for obtaining smaller mean particle size value as compared to the ones reported by Koroleva et al. may be related to the effect of aqueous silica nanoparticles on the mean particle size as explained above. Koroleva *et al.* ,2017 also searched for possible enhancement in the emulsion quality with addition of nano-ceramic particles (Ludox CL, alumina coated silica, average diameter: 20 nm) with ratios of 0 to 2%wt. It was observed that the mean diameter of the dispersed paraffin

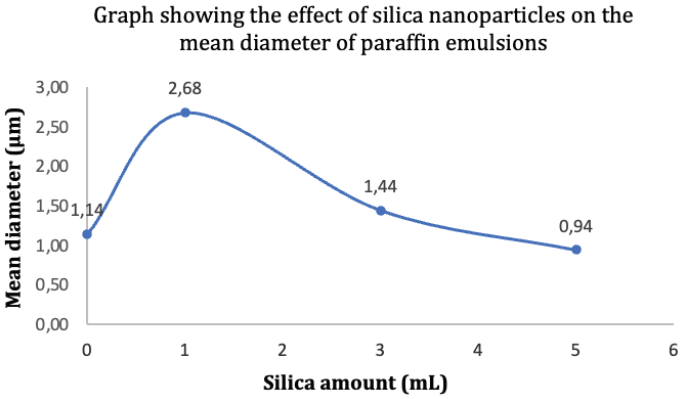
increased with the increment of the nano-ceramic quantity. These results are partially in accordance with the ones obtained in the present work, however, the mean diameter was observed increased initially and later decreased with further increasing the aqueous silica nanoparticles amount in the present study (Figure 5(a)).

Contact Angle Measurements

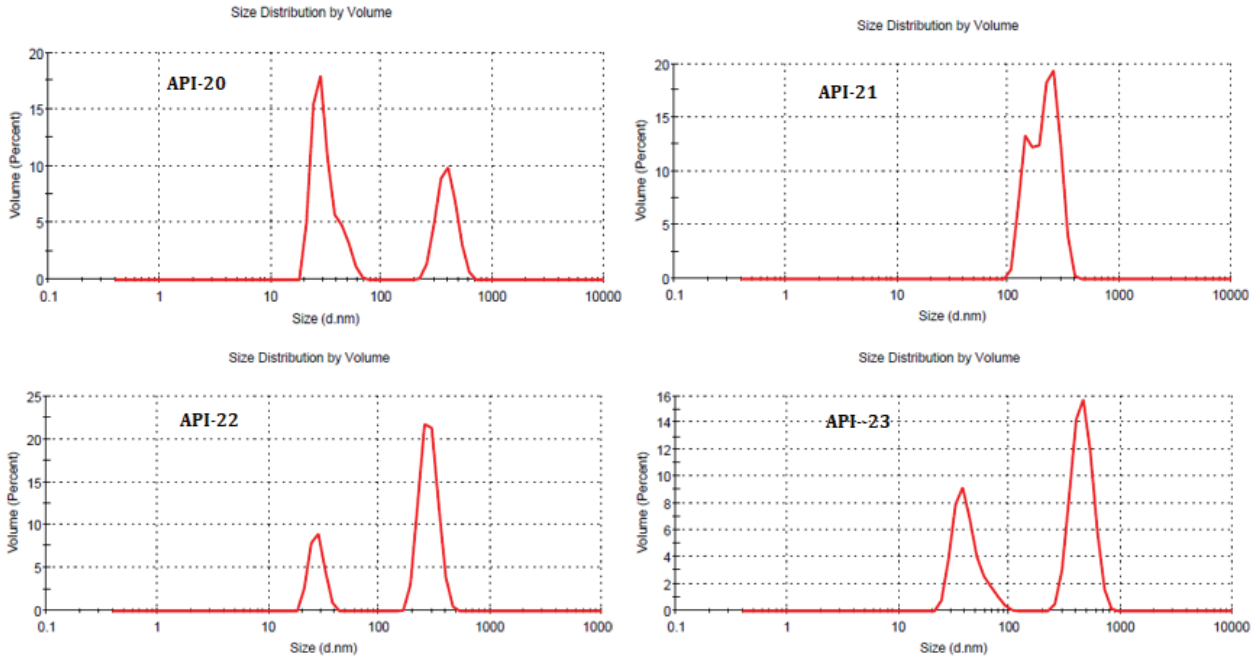
Measuring the contact angle provides knowledge on the successfulness and achievement made by preparing the emulsions. One of the main application sectors of paraffin wax emulsion is the manufacturing of forest products e.g. (MDF, HDF, Chipboards etc.) to provide water repellent ability. The basic technique to analyze how well a surface is hydrophobic is by measuring the angle that is formed when a specific volume of water (10 μL) drop is released onto it. The results obtained after measuring the contact angles of the samples have been presented in Table 3.

Table 3. Results of contact angle measurements

Sample	Contact Angle (°)
PW	104
30 % PWE	90.5
40 % PWE	96.8
50 % PWE	98.8
60 % PWE	102.6



(a)



(b)

Figure 5. Image displaying results of the four samples about the influence of aqueous silica nanoparticles on (a) emulsions' mean diameter and (b) particle size distribution graphs (volume-based).

All the contact angle measurements were performed by using the Image J application. According to the results, all surfaces coated with different paraffin wax emulsions proved hydrophobic. The higher the paraffin wax content applied in the emulsion, the more hydrophobic the surface becomes. Results obtained were acceptable because one of the targets is to make materials gain water-repellent (hydrophobic) characteristics when applied with paraffin emulsions. The results exhibited by all the samples (30%, wt. PWE, 40 % wt. PWE, 50%wt. PWE and 60 %wt. PWE) were quite convincing since they were below that of PW sample (104°) as expected. The lower contact angles of the emulsion samples than that of pure paraffin wax can be associated with the presence of emulsifier in the emulsions. Generally, emulsifiers are amphiphilic, they possess both water-loving part and oil-loving part at the same time. This water-loving part plays a role in the reduction of the contact angles of the emulsion samples. However, considering the ease of application, handling and effectiveness, emulsions would be generally preferred to molten paraffin waxes. The images captured from Image J application during the contact angle measurement can be seen below (Figure 6).

Effect of Different Emulsifier on the Stability of the Paraffin Wax Emulsion

PEG-7-Glyceryl Cocoate is an emulsifier that helps stabilize and thicken formulas by reducing the surface tension between the phases to be emulsified. It has hydrophilic-lipophilic balance (HLB) value of 10. Effect of different emulsifiers, IK-8000 and PEG-7-Glyceryl Cocoate on the stability of the formulated paraffin wax emulsions was studied. Samples of the emulsions prepared with each emulsifier

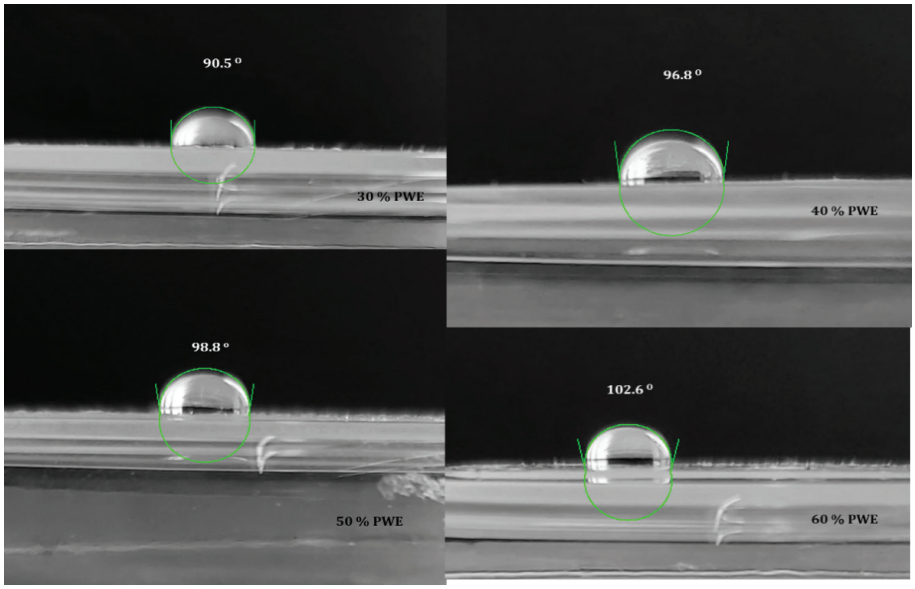


Figure 6. Results of contact angle measurements of; 30%wt. PWE, 40 %wt. PWE, 50%wt. PWE and 60%wt. PWE samples.

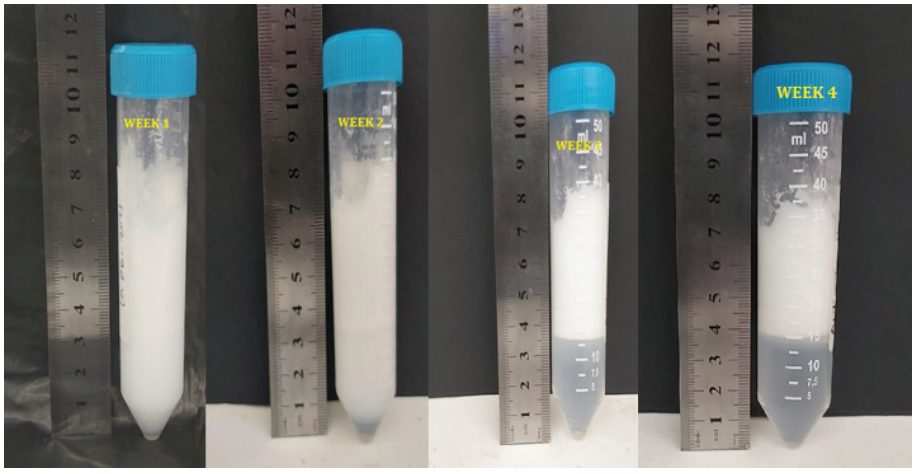


Figure 7. Images of PEG-7-Glyceryl Cocoate stabilized emulsions taken during stability analysis.

was stored and observed for a month. The images taken during the observations have been presented in Figure 7.

It was observed that phase-separation started occurring in the PEG-7-Glyceryl Cocoate stabilized emulsion after 3 days of preparation whereas those prepared with IK-8000 emulsifier remained stable for the one-month observation. The reason for the phase-separation of emulsion stabilized with PEG-7-Glyceryl Cocoate emulsifier can be related to the length of the monomers in this emulsifier. Despite having its HLB value (10) in the range appropriate for stabilizing paraffin wax emulsions, the short length of its monomers was not suitable and cannot reduce the interfacial tension between the phases nor provide the stearic effect needed to keep the dispersed phase apart. It was able to form the paraffin wax emulsion but cannot hold the dispersed particles apart for longer time. Due to this reason, PEG-7-Glyceryl Cocoate emulsifiers are mostly applied as stabilizers in body and hand lotions. They can also be used to emulsify vegetable oils without any potential problems because oils have lesser carbon chains than paraffin wax. From the results observed, the PEG-7-Glyceryl Cocoate stabilized emulsion's percentage stability was calculated to be 66.7 %/month using equation 1.

Mean Diameter Analysis (MDA)

A typical dynamic laser light scattering (DLS) analysis result for the sample (17.5%wt. paraffin, 2.5%wt. IK-8000, without adding silica nanoparticles) is shown in Figure 8. The mean particle size was determined to be 1026 nm for the polydisperse emulsion. The polydispersity nature of the emulsions may be caused by the high content of the paraffin wax dispersed which was also reported by Koroleva *et al.,2017*. The DLS analysis was performed without diluting the samples in order to monitor the "as it is" situation of the prepared emulsion, unlike in the previous studies by Liu *et al.*,2006 and Xin *et al.*, 2013, where the samples were diluted 1000 and 500 times, respectively. Diluting the prepared samples with deionized water changes the concentrations of its components (paraffin & emulsifier) and their relative ratios. This will result in the formation of a new sample which may hardly have similar properties as it had before the dilution. Liu *et al.*, 2006 reported the droplet diameters values to be in the range of 160 – 6600 nm for 20%wt. paraffin oil and 5 % emulsifier (mixture of Tween 80 and Span 80 with varying ratios) after diluting the samples for 1000 times. Xin *et al.*, 2013 also used a mixture of emulsifiers (Span 20 & Tween 20) in their studies and determined the effect of emulsifier mixture content (3-10%wt.) on particle size and particle size distribution [27]. They reported that increasing the emulsifier mixture content in the emulsion (3-10%wt.) decreased the mean diameter value and also resulted in the formation of emulsions with less polydispersity. The mean particle size reported at higher emulsifier amount (3-10 %wt.) was in the range of 133 to 323 nm and these results were obtained after diluting the samples 500 times. It was also mentioned that further decrease in mean diameter values was possible (e.g. 120 nm) when ionic surfactants (SDS and CTAB) were used. When compared to the mean diameter value obtained in this study, the value reported by Koroleva *et al.*, 2017 were bigger (~5800 nm for 20%wt. paraffin and 1 % emulsifier) while that reported by Liu *et al.*, 2006 was within range (160-6600 nm for 20%wt. paraffin oil and 5 % emulsifier mixture). However, the mean diameter value reported by Xin *et al.*, 2013 (133 to 323 nm for 20%wt. paraffin oil and 3-10 % emulsifier mixture) was smaller than the one obtained in this study. The relatively higher paraffin wax content used (e.g. ~20%wt.) and the performance of size distribution analysis without samples dilution may be the main reasons for obtaining polydisperse emulsions. Dynamic Laser Light Scattering (DLS) instrument was used to determine the particle size distribution. The intensity of the scattered light was monitored and the mean diameter of the particle/droplet was determined via Stokes-Einstein equation by considering the Brownian motion of the particle/droplet. The scattered light's rate of intensity variation may be further used for the determination of particle size distribution (PSD). The particle size distribution analysis results can be presented based on the number and/or volume of the particles/droplets. This analysis doesn't give accurate results for samples with higher polydispersity; however, it may provide some clues about the size distribution. The PSD graphs can be relatively different from each other, as can be seen in Figure 8 (a) and (b) since the number-based distribution is related with D (particle/droplet diameter) while the volume-based distribution is related with D^3 (Cubic). In the number-based distribution graph given in Figure 8 (a), almost all particles are in the range of 20 to 100 nm with a mean value of 49 nm. There is another peak with a mean diameter of 439 nm which is hardly visible on the number-based graph (Figure 8 (a)). Nonetheless, considering the volume-based distribution (Figure 8 (b)), a peak depicting larger particles was observed within the range of 200-900 nm (with a mean value of 470 nm). The ratios of particles in the range of 20-100 nm and 200-900 nm was 37% and 63%, respectively. The hydraulic diameter (mean diameter) determined via Stokes-Einstein equation was 1026 nm for the polydisperse sample. This value gives information about the presence of relatively bigger particles in very small ratio which were not observed as a different peak on either of the PSD analysis (number-based or volume-based). The PSD analysis shows that the emulsion samples prepared with relatively high paraffin content were polydisperse and are composed mostly of nanoparticles in the ranges of 20-100 nm, 200-900 nm and a few bigger particles in a very small ratio. These results are more convincing than the most of previously reported results in the literature considering the fact that all measurements were done without any form of sample dilution and higher paraffin/emulsifier ratio used.

The main application area of paraffin wax emulsion is the manufacturing of forest products like; chipboard, Medium Density Fiberboard (MDF), High Density

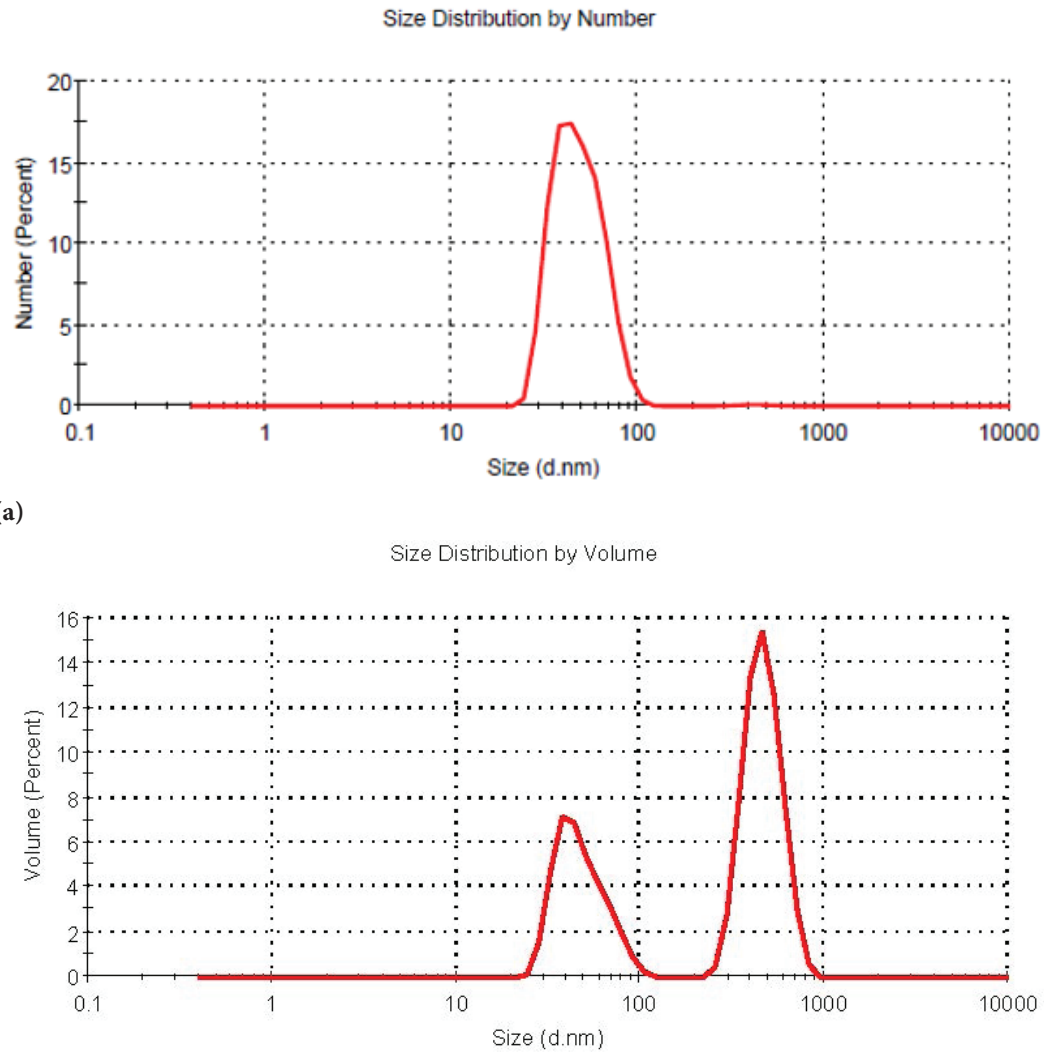


Figure 8. Particle size distribution (PSD) analysis result for the sample with 17.5 %wt. paraffin, 2.5 %wt. emulsifier, (a) number-based distribution, (b) volume-based distribution.

Fiberboard (HDF) and etc. in which paraffin wax emulsion is added at the point of mixing during the production processes to make sure they are evenly spread within wood particles. The paraffin particles then melt at temperature above its melting point and form a hydrophobic film on the surface when the boards are finally formed by pressing under high pressure. Paraffin wax emulsion with smaller particle size would provide a higher surface area to cover the wood particles.

CONCLUSION

Paraffin wax emulsions with varied solid contents (20-60 %wt) have been successfully produced and characterized. The mean diameter of the emulsion was determined to be around 1.026 μm. Moreover, it was observed that despite PEG-7-Glyceryl Cocoate emulsifier having HLB value of 10, which is a suitable for emulsifying of paraffin waxes, it was not able to stabilize paraffin wax emulsions produced for longer period. This means that not only HLB value but also the type and nature must be considered when choosing an emulsifier. Furthermore, it was seen that the addition of aqueous silica nanoparticles had positive influence on the emulsion's stability. The emulsions which were stabilized with both IK-8000 and silica nanoparticles; API-8, API-9, API-10, API-11 and API-12 remained stable for more than 2 months. This was related to the stabilization properties from both the IK-8000 emulsifier and the aqueous silica nanoparticles. The addition of aqueous silica nanoparticles also had a significant effect on the mean particle size of the emulsion. It was observed that increasing the content of aqueous silica nanoparticles (1.0-5.0 mL) initially increased

from 1.142 μm to 2.680 μm then decreased the mean diameter of the paraffin wax emulsions to 0.942 μm. The addition of a 1.0 mL of silica nanoparticles to the emulsion, those silica particles were adsorbed on the surface micelles thereby causing an increase in the mean particle size of the emulsion. The contact angle measurement results of the emulsions proved that they can provide hydrophobic property to the products they are applied. It should be noted that paraffin wax emulsion with very small mean particle size can be produced by controlling the stirring speed and rate of water-addition to the oil phase. Also, the effect of pH on the mean particle size and stability of the paraffin wax emulsion should be investigated further.

ACKNOWLEDGMENTS

We, the authors express our gratitude to Prof. Dr. Kerim YAPICI for providing silica nanoparticles which was used in this study. We thank Dr. Kasım AKSOY for assisting us with devices for the research. Finally, we acknowledge the Department of Scientific Research Projects (BAP) of Süleyman Demirel University for the financial support via the project with the code FYL-2020-8136.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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