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**INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH**

RESEARCH ARTICLE

Characterization of nanoparticles stabilized food emulsion and its adhesion to packaging sheets

Saber A. Ibrahim[1], Omar R. Soliman[1,2,*]

1. Packaging Materials Department, National Research Centre, Dokki, Cairo, Egypt
2. Chemistry Department, Jazan University, Kingdom of Saudi Arabia

Manuscript Info	*Abstract*
  *Corresponding Author Corresponding author: Tel.: 009660583646844 E-mail address: omarsoliman246@yahoo.com (Omar R. Soliman)	The competition between companies provides an outstanding importance to study the problem of food emulsion. Especially emulsions that stabilized by particles, of higher stability, which are of lower price than the corresponding emulsifiers. Adhesion to their contact surfaces is of unlimited goal to clean the packages with the least cost. A study of emulsions stabilized by nanometer-sized silica particles alone (trade name; Nalco 1060, Ludox AM30, Ludox AS40, Ludox Sm30 and Ludox TM50) were performed to determine the best silica particles for edible emulsion stabilization. Bulk adhesion was experimentally measured by weighing the remaining food emulsion on solid surfaces after contact (i.e., adhesion amount).A series of different emulsions of (corn, olive, soya bean and sunflower oils) which stabilized by silica particles were prepared to study the effect of using surfaces of different hydrophobicity. Polypropylene, polyester and glass were used as packaging surfaces that are of different philicity.

1. Introduction

Emulsions are liquid in liquid dispersions that form an important class of products used in food and pharmaceutical industry. The preparation of food products with the least adhering amount to surfaces is absolutely of high economic value. The product quality decreases sharply by the presence of food remaining on the packaging film. Moreover, it increases the cost of packaging surface cleaning by increasing the recycling cost of the used packaging materials.

An increasing attention is being dedicated for the so-called Pickering emulsions or generally solid stabilized emulsions in food applications. Solid particles have been widely used in emulsion formulations including those of the food industry (Aveyard et al., 2003). Additionally, (Dickenson, 2010) have described a numerous applications of particles for stabilization of edible emulsions and edible foams (eg. whipped dairy cream and dessert toppings and ice cream).This interest results from their extreme advantageous over conventional emulsions. Solid particles of nanometer size range are capable of stabilizing emulsions in absence of surfactant, are well known (Aveyard et al., 2003; Binks and Lumsdon, 1999; Binks, 2002; Arditty, 2004). In different ways, particles behave like surfactants as emulsion stabilizers. Silicone nonionic emulsifiers were used to prepare a non-flammable and non-toxic silicone emulsions that are environmentally safe to be used in large scale.

Silicone Emulsion meets FDA CFR specification for use in food contact surfaces.

For determination of the type (oil-in-water, o/w, or water-in-oil, w/o) and stability of the formed (surfactant stabilized) emulsions when oil, water and stabilizer are homogenized, hydrophile/ lipophile balance (HLB) is the most important variable used. For emulsions stabilized by particles, particles wettability is the best

important variable used for determination of the type (oil-in-water, o/w, or water-in-oil, w/o). Particles to be adsorbed at the interface need to be partially wetted by both phases (oil, air or water). The contact angle (the angle between the particle tangent at contact and the interface, through the water phase, Fig. 1) is the relevant parameter. For a preferentially oil wetted particle the contact angle is larger than 90°, while it is smaller than 90° for water wetted particles. It is empirically stated that the phase that preferentially wets the particle becomes the emulsion continuous phase. Hence O/W emulsions (continuous phase is water) are obtained for contact angles smaller than90^o, and W/O emulsions (continuous phase is oil) are those obtained for contact angles greater than90^o (Binks and Lumsdon, 2000). The desorption energy **E** (the energy required to remove a particle from the interface) can be estimated simply through the following relationship.

$$E = \gamma_{int}\pi R^2(1 - |cos\theta|)^2 \qquad\qquad (1)$$

Where γ_{int} is the interfacial tension of the interface and R is the particle radius. The adsorption and desorption energy of a surfactant molecule at the interface is of the order of k_BT (k_B is Boltzmann constant), while it can easily reach several thousands of k_BT for nanometric particles (characteristic of fumed silica particles). Subsequently surfactant molecules are in dynamic equilibrium between interface and bulk whereas particles are irreversibly adsorbed at the interface. This difference is at the origin of distinctive properties of solid-stabilized emulsions (Arditty et al., 2003, 2004, 2005; Binks, 2002; Binks and Lumsdon, 2000).

It is well known that Emulsion stability is a kinetic concept. For stable emulsions, there is no apparent change in the number of drops, their size distribution or their spatial arrangement within the experimental time scale. The recognized Emulsion instability includes four main ways in which an emulsion may become unstable. These different ways are creaming (or sedimentation), flocculation, coalescence and Ostwald ripening and were reviewed by(Curt, 1994,).Creaming result from the effect of gravity on drops of lower density than that of the continuous phase. In case of dilute emulsions, the creaming speed (V) of an isolated, spherical drop of radius (r) moving through a fluid medium of density (l_o) and Newtonian shear viscosity (η) is given by Stokes' Law as in equation (2).

$$V= \frac{2gr^2(lo-l\ \ )}{9\eta} \qquad\qquad (2)$$

L is density of dispersed phase and g is acceleration due to gravity. Moreover, adjusting the viscosity of the dispersion medium by adding thickener to the aqueous phase often leads to non-Newtonian character of the continuous phase. Therefore, a complication in applying equation 2 is expected.

Adhesion resistance against separation of two materials which are adhered together for a period of time at a certain temperature is of major importance in many industries. For food industry, adhesion of food into the packaging surfaces may reduce the product appearance and increase the product loss (Criado et al., 1986) consequently increase the package recycling costs. Moreover, the products adhesion to equipment surfaces will increase the cost of cleaning process.

Adhesion of oils and emulsions on different packaging materials and surfaces like stainless steel and glasses have been studied (Michalski et al., 1999).The problem of adhesion of emulsions arises from their fatty nature and they contain hydrocolloids as stabilizers that are likely to adsorb on surfaces. This category contains many sauces and dressings.

Many researchers reviewed food materials adhesion to industrial equipment and packaging surfaces (Michalski et al., 1997). As well as, there are many studies have been applied to this topic and were applied to specific food products (Saunders et al., 1992; Nishino et al., 1990). Moreover, many scientists used the thermodynamic adsorption theory of adhesion but for specific food ingredients, such as proteins, rather than for actual food products (McGuire and Kirtley, 1988; McGuire and Kirtley, 1989; McGuire, 1990; Krisdhasima et al., 1992). Regarding food contact surfaces (Boulange et al., 1993) studied the theoretical adhesion approaches for sanitary purposes concerning the adhesion of microorganisms. The adhesion of simple fatty food products and the bulk adhesion of concentrated food emulsions with mayonnaise-like composition stabilized with lecithin (Michalski et al. 1998) and whey protein isolates (Michalski et al. 1999) have been studied.

The aim of the current study is to evaluate the bulk adhesion of concentrated food emulsions on packaging material after drainage flow. These emulsions are of a mayonnaise-like composition, stabilized with the best stabilizing particles of the available colloidal silica series and collagen as thickener. It extended to find surface and emulsion parameters responsible for bulk deposits adhered on surfaces after flow (adhesion amount, M_{ad}).

2. Materials and method
2.1 Materials:

The selected five colloidal silica particles for investigation are obtained from DuPont and were selected to reflect a range of sizes and surface chemistry, namely, LUDOXSM30, AM30, AS40, TM50 and Nalco1060 of radius 3.5 nm, 6 nm, 11 nm, 50 nm and 60 nm, respectively. SM30 at pH 10.2,contains 30% SiO_2, stabilizer, and at 25 °C the macroviscosity is 5 cP; AM30 at pH 8.9, contains 30% SiO_2, trivalent aluminum ions substituted for some of the tetravalent silicon ions on the surface, 0.24% stabilizer, and at 25 °C the macroviscosity is 11 cP; AS40 has a negative particle charge at pH 9.2, contains 40% SiO_2, and at 25 °C the macroviscosity is 9 cP (Apperson et al., 2009) other specifications was tabulated in Table 1. All the LUDOX samples studied have free hydroxyl groups tethered on the outside of the nanoparticle and capable of binding to water, potentially increasing the measured hydrodynamic radius. LUDOX is quite stable, but its repeated exposure to atmospheric CO_2 has the effect of lowering the pH, eventually resulting in gelation. Monodisperse hydrophilic silica particles (Nalco 1060, Ludox AM30, Ludox AS40, Ludox Sm30 and Ludox TM50 from Aldrich) were used as received as an aqueous suspension. These particles are stabilized at high pH to prevent irreversible coagulation.

Different oils (corn, olive, soya bean and sunflower) were used as received from Aldrich, Germany. Polymer sheets, polyester F-CHC from Flexpet, France and polypropylene HS from Gulf Pack, KSA,Glass and Aluminum sheet (mainly used in beverages packaging)were chosen for their extensively use in food packaging. Deionization of a distilled water source was performed using a milli-Q reagent water system (to give water with a resistivity of 18 MΩ cm).

2.2 Characterization:

- Particle size of silicon colloids were measured with Nano-ZS(Malvern Co., UK) with measurement range 0.3 nm – 10.0 microns (diameter), Light source He-Ne laser 633nm, Max 5mW and minimum sample volume 12 µL was used to measure the particle size of prepared latex.
- Conductivity was measured with HI 98130, Waterproof pH, EC/TDS & temperature meters, Hanna Instruments Inc., USA.
- The viscosity was measured using brookfield Viscometer, Brookfield DV- III Ultra Viscometer (Brookfield, USA), The viscometer reside in a Polyscience constant-temperature, water bath controlled within ±0.01 K. The attached digital thermometer was used to measure the temperature with an accuracy calibration.

2.2. A. Preparation and characterization of emulsions:

A mix of 5ml of water (the dense phase) was added first to test tube then 1% suspended silica (Nalco 1060, Ludox AM30, Ludox AS40, Ludox Sm30 and Ludox TM50)then followed by 5ml of vegetable oil (corn). Using an IKA Ultra-Turrax T25 homogenizer (the Ultra-Turrax was fitted with a dispersing head of diameter 18 mm) for homogenisation, it took place at 4000 rpm for 5 minutes.The continuous phase was inferred by (drop test) observing whether a drop of emulsion dispersed or remained when added to either the pure oil or pure water emulsion (Binks, 2002). Water continuous emulsions (oil-in-water, o/w) prefer to disperse in water and remain as drops in oil, while oil continuous emulsions (water-in-oil, w/o) prefer to disperse in oil but remain as drops in water. For conductimetric measurements, Hanna Instruments HI 98130 conductivity meter was used to determine the conductivity of emulsion. Conductivity measurements were made immediately after homogenization. Low conductivity values were related to oil continuous emulsion, while high conductivity values were attributed to water continuous emulsion (Binks, 2002). Stability monitoring of water continuous emulsions to creaming and coalescence was determined by monitoring the change with time of the water-emulsion boundary and oil-emulsion interface respectively. Meanwhile, for oil continuous emulsions, the stability to sedimentation and coalescence was determined by monitoring the change with time of the oil-emulsion boundary and water-emulsion interface respectively.

2.2. B. Preparation and characterization of emulsions (corn, olive, soya bean and sunflower oils) stabilized by the best silica type:

As we used hydrophilic silica particles it is predicted that all emulsions will be oil-in-water (o/w). For each set oil percentage was 70%, silica was 1% and protein was 1.5% according to the industrial proportions (Michalski et al., 1999). Water, silica and protein were mixed by gently stirring using an IKA Ultra-Turrax T25 homogenizer. The dispersing head of the homogenizer was immersed in the mixture prior to homogenization at the

specified temperature (emulsions were thermostated at 25 ± 1°C) for 10 minutes. The homogenization took place at 4000 rpm for 5 minutes.

2.3   Emulsion adhesion to packaging film:

The amount of adhered emulsion to the packaging film (W_{ad}) is measured using a simple designed device as shown in Fig. 2, The prepared edible emulsion was held back at the middle to of a 80° tilted surface (polypropylene and polyester films, glass and aluminium). Subsequently it was allowed to flow down and the weight remaining on the film surface after flow had stopped was measured using four digital precision balance, so that:

$$W_{ad} = (depositweight\ (solidweightbeforeflow - solidweightafterflow)\ )/(surfacearea)(g.m^{-2})$$

3.   Results and Discussions

3.1. Determination of emulsion viscosities and emulsion type by drop test and conductivity:

All silica particles series are used as received from the supplier and were wetted by water i.e dispersed in water. Consequently, all emulsions were in the form of oil in water (o/w) emulsions. Moreover, it was proved by drop test and conductivity measurements in table (2).

3.2 Stability of O/W emulsions to creaming (water resolved):

As it is concluded from the drop test and conductivity results (in table 3) all the prepared emulsions were o/w. According to (Ashby and Binks, 2000), the stability of o/w emulsions to creaming was assessed by monitoring the increase with time of the position of the water, as shown in (Fig. 3). As it is found in Fig. 3, the stability of emulsions to creaming was decreased as a result of increasing water resolved by time. The highest emulsion stability to water resolved was those emulsions prepared by Ludox Sm 30 (the lowest rate of resolved water) then those prepared by Ludox TM50, Ludox AM30, Nalco 1060 and Ludox AS40 respectively. Furthermore, these results are in coincidence with viscosity results in table (2) as there is no any added thickener which increases the emulsion viscosity. Where the inverse relation between creaming speed (V) of an isolated, spherical drop and the viscosity in stokes' law means that the highest emulsion to creaming (lowest creaming speed) will be of the highest viscosity. In other words, the emulsion prepared by Ludox Sm 30 will be of higher stability (lowest creaming speed and highest viscosity) and that prepared by Ludox AS40 will be least stable emulsion (highest creaming speed and lowest viscosity).

3.3 Stability of O/W emulsions to coalescence (oil resolved):

According to previous results, all the prepared emulsions were o/w. The stability of o/w emulsions to coalescence which was assessed by monitoring the increase of oil position with time was studied (Binks et al., 2005) (Fig. 4). In Fig. 4, it is obvious that the stability of emulsions to coalescence decreases as a consequence of increasing rate of oil resolved by time. The highest emulsion stability to water resolved was those emulsions prepared by Ludox Sm 30 (the smallest rate of resolved oil) then those emulsions prepared by Nalco 1060, Ludox AM30, Ludox TM50and Ludox AS40respectively.

3.4 Stability of O/W emulsions:

As shown in Fig. 5, the stability of the prepared emulsions (according to relative volume of emulsions after discarding resolved oil and water) decreases with an increase of the time after emulsions preparations. This stability was in the following order Ludox Sm30, Nalco 1060, Ludox AM30, Ludox TM50and Ludox AS40respectively. Moreover, those results are in coincidence with results obtained from Fig.3 and Fig.4. Finally, it clear that it is advisable to use Ludox Sm 30 as particles for emulsion stabilization and it will be used for this purpose to study the adhesion of food emulsions to packaging.

3.5 Relation between viscosity of oil [(olive, corn, soya bean and sunflower)-water, emulsion system] that stabilized by Ludox Sm 30 and their emulsion stability:

As it is well known from stoke's law that Adjusting the viscosity of the dispersion medium is normally achieved by thickening the aqueous phase, always result in a non-Newtonian character of the continuous phase and hence a complication in applying equation 2. Thereforethe addition of collagen as a thickener will result in that difficulty as it is shown in Fig.6. Meanwhile, it is important to study viscosity of the prepared emulsions over a range of temperature. This will support food emulsion study during production, transportation and shelf temperature. Fig. 6 shows the relationship of viscosity vs. temperature for the selected four edible oil emulsions.

As illustrated in actor lines, viscosity was decreased with temperature increase over range from 25 to 50 ^{o}C. Viscosities of different prepared emulsions like-Mayonnaise were ordered with fixed arrangement, Sunflower, Corn, Olive and soybean oils, at different temperature. Overall, food emulsions were affected with working temperature with decrease in viscosity which can be applied in food emulsion industries to decrease energy lost to have green environment.

3.6 Effect of philicity of packaging film on the amount of adhered emulsions:

According to surface philicity,as it is shown in Figures (7, 8, 9 and 10) the investigational adhesion was found to decrease with increasing hydrophilicity of the packaging film, therefore the adhered emulsion to hydrophobic films (pp and PS) was generally greater than hydrophilic films (aluminum film and glass). This is may attributed to a competition between protein and silica particles, where the protein has more hydrophobic sites and consequently its desorption energy is expected to be greater (in case of contact with hydrophobic film), which means that the surface will be covered more by proteins than by silica particles. In contrast, the adsorption of protein on hydrophilic, high-energy surfaces is lower than that of silica particles. Moreover, the effect of different viscosities for the prepared emulsions of different oils was of less magnitude than the effect of philicity of the packaging film.

Figure 1: Illustration of the contact angle Ө for a particle adsorbed at oil-water interface. (a) particle more like water (Ө < 90°) or water wetted particle (b) particle more like oil (Ө > 90°) or oil wetted particle
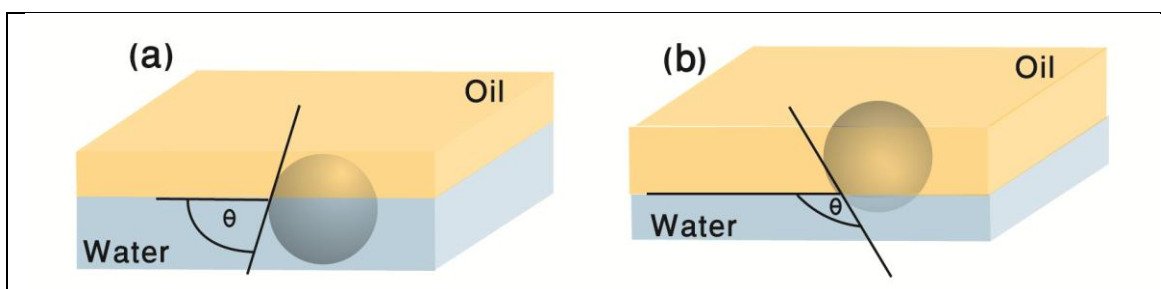
Figure 2:   Cartoon of designed device for measuring amount of emulsion adhered (M$_{ad}$) at 25±1°C: (a) product release, (b) product flow and determination of the end of flow time and (c) weighing of the remaining residues.
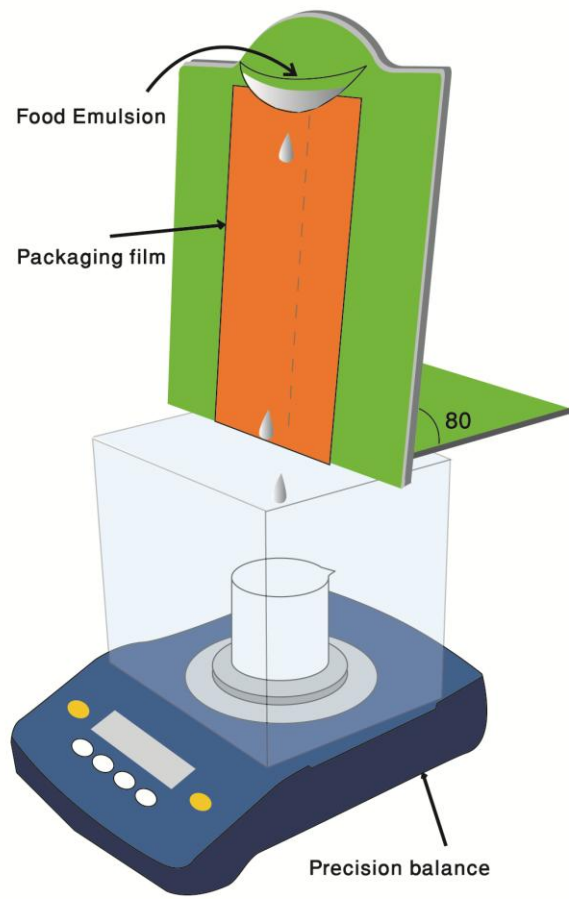

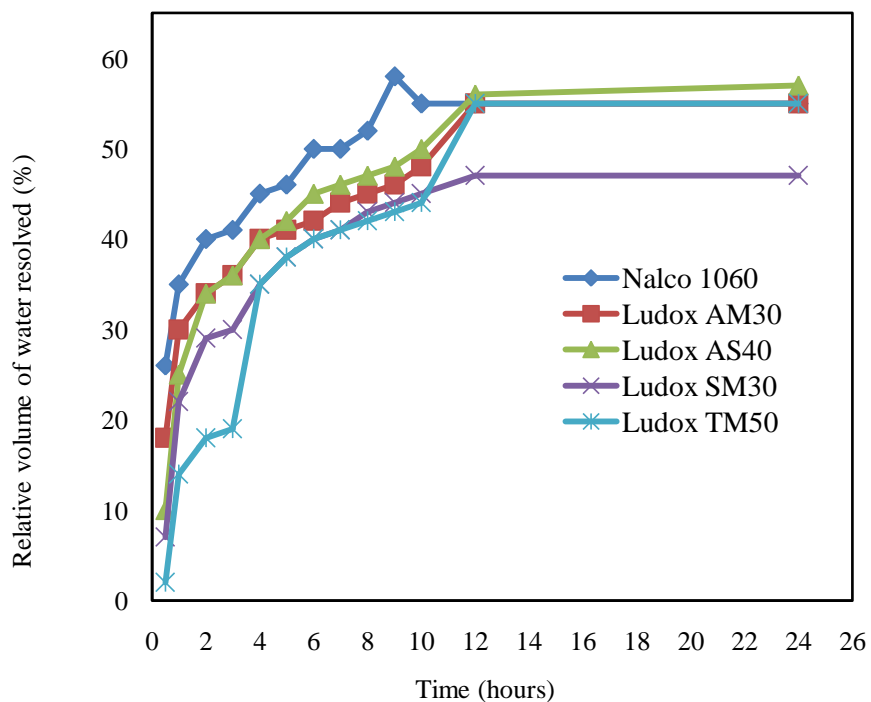**Figure 3: Effect of silica particles on creaming rate**

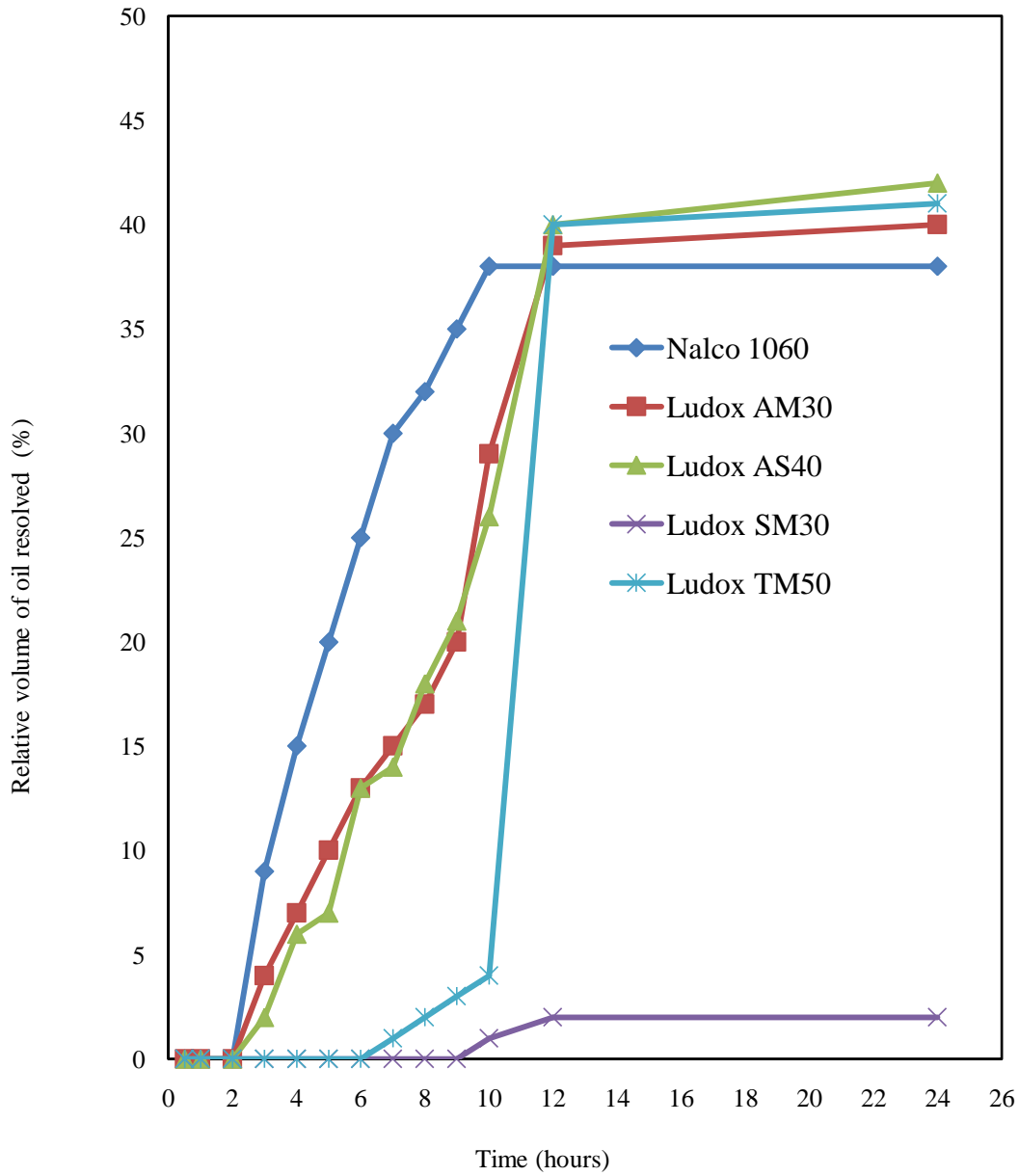**Figure 4: Effect of silica particles on coalescence rate**
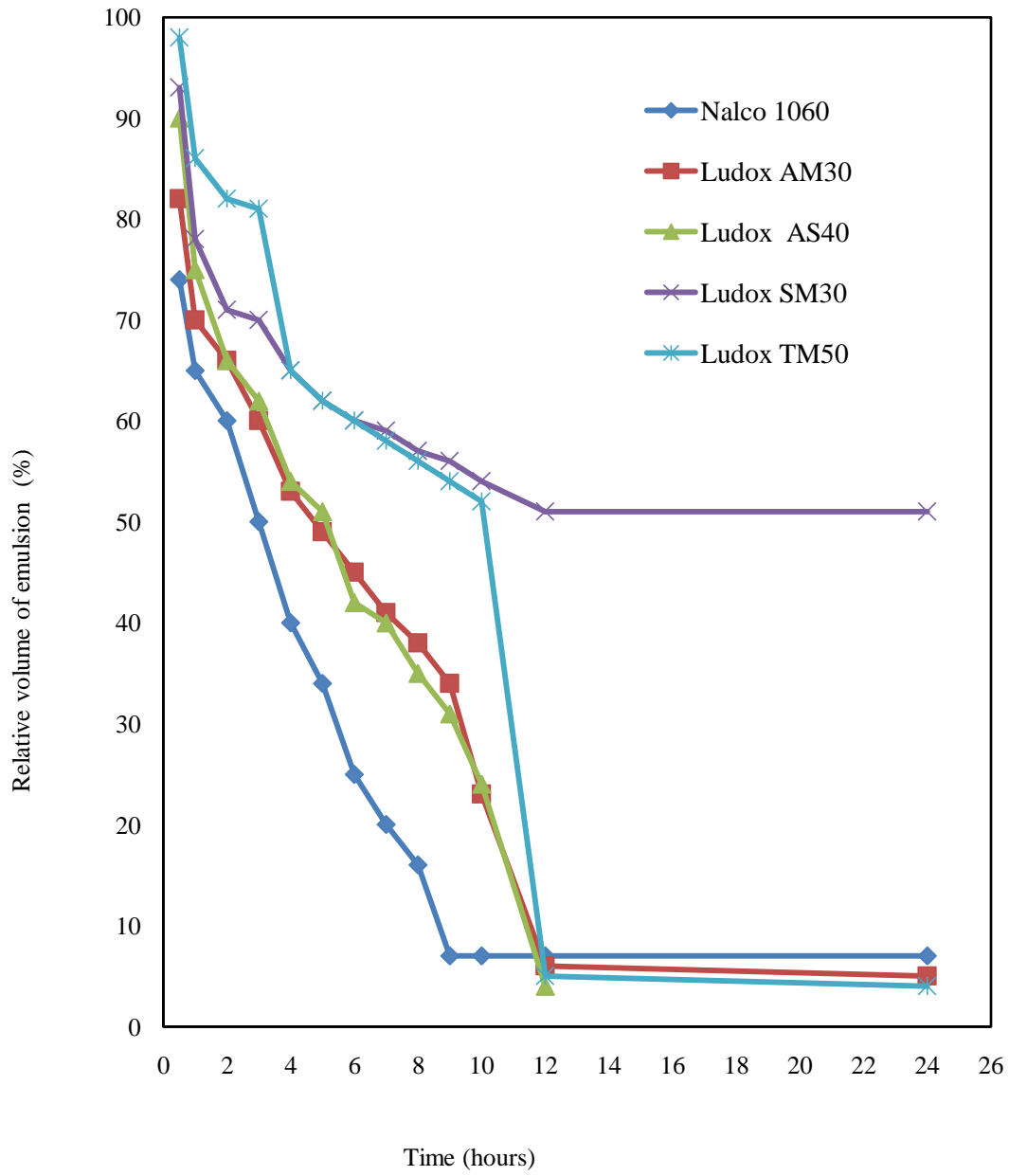
Figure 5: Effect of silica particles on emulsion stability

Figure 6: Effect of temperature on viscosity of oil (olive, corn, soya bean and sunflower)-water, emulsion system, that stabilized by Ludox Sm 30
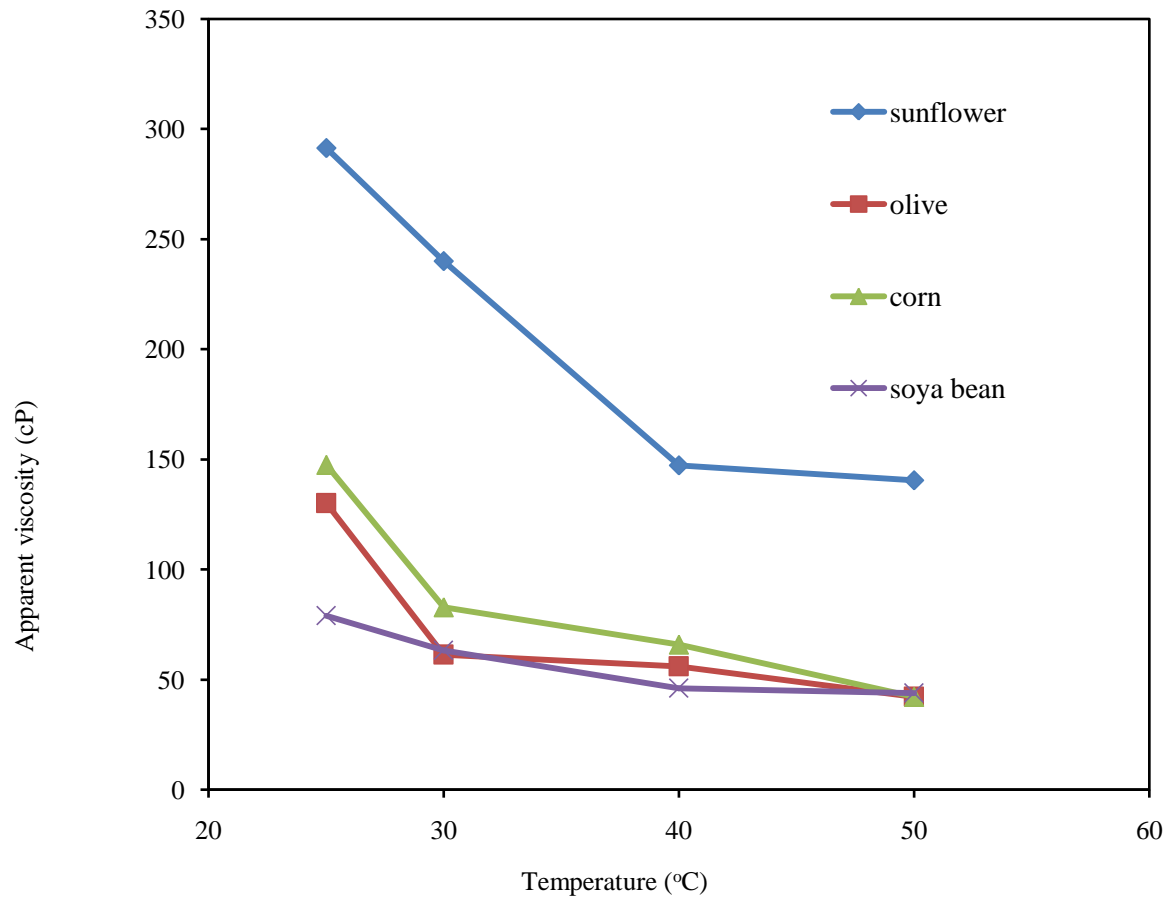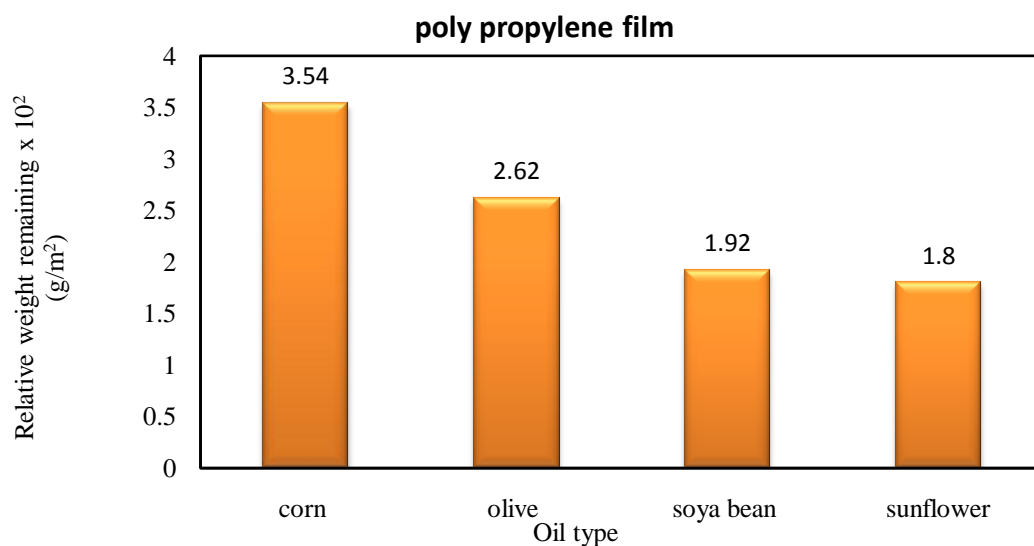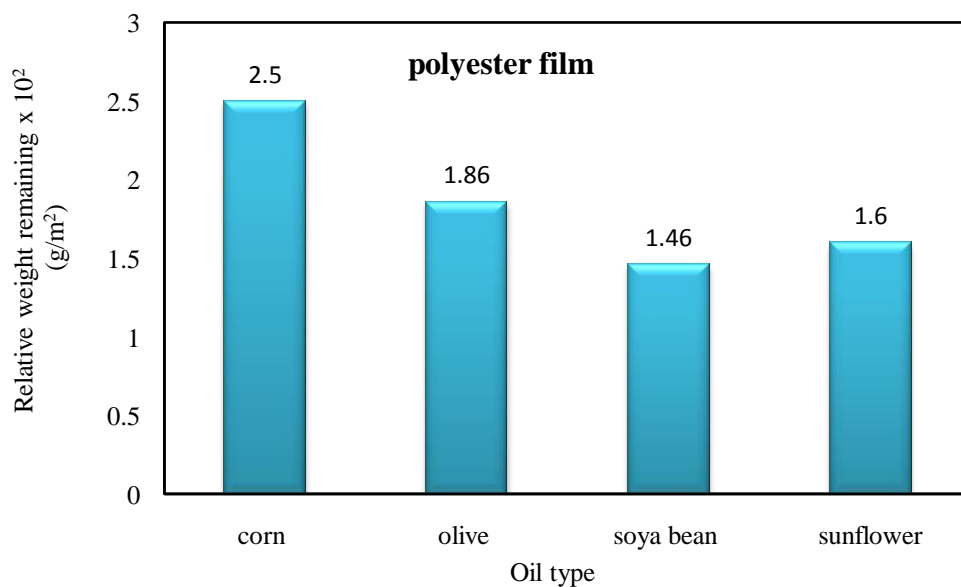
Figure 7: Effect of non-polar (polypropylene) film on the adhesion (g/m^2)

Figure 8: Effect of polar (polyester) film on the adhesion (g/m^2)

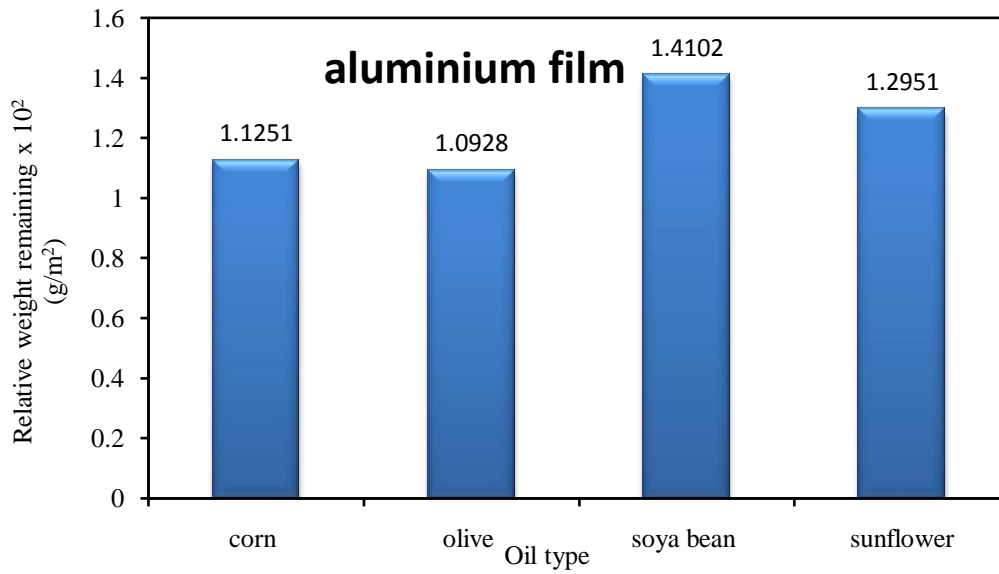**Figure 9: Effect of polar (aluminum) film on the adhesion (g/m^2)**

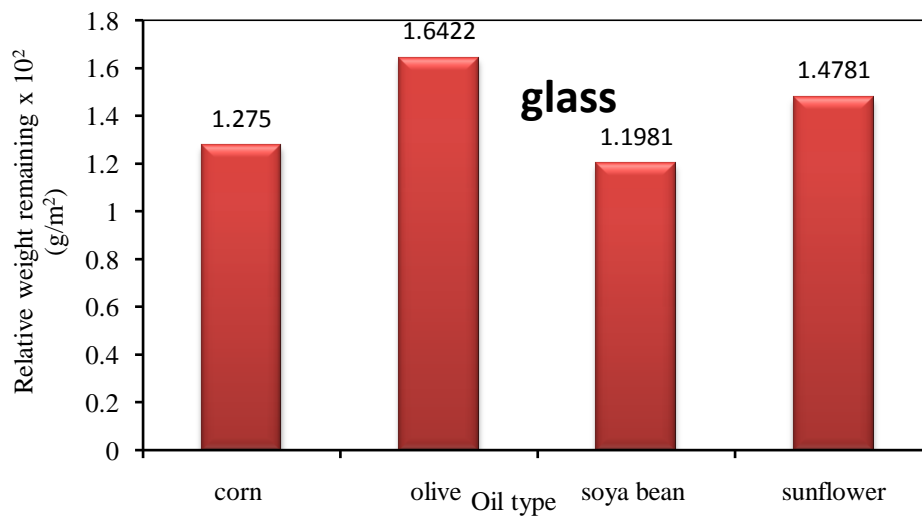**Figure 10: Effect of polar (glass) film on the adhesion (g/m^2)**

Table 1: Characterization of silica particles series

Emulsifier	Concentration, wt.%	pH	Surface area, m^2/g	Density, g/ml	Particle size, nm
Nalco 1060	5	8.7	~119	0.91	61
TM50	50	9.0	~140	1.4	49
AM30	30	8.6-9.3	198-250	1.21	6.2
AS40	40	9.1	~135	1.29	11.5
SM30	30	9.7-10.3	320-400	1.22	4.1

Table 2: Identification of emulsion viscosity - emulsion type by drop test and conductivity measurements of vegetable oil (corn-water emulsion system) that stabilized by different silica particles.

Type of Silica	Drop test	Viscosity, Cp	Conductivity, µs	Emulsion type
Nalco 1060	Disperse in water and remains as drops in oil	5.6	700	O/W
Ludox AM30	Disperse in water and remains as drops in oil	5.9	400	O/W
Ludox AS40	Disperse in water and remains as drops in oil	5.0	390	O/W
Ludox Sm 30	Disperse in water and remains as drops in oil	11.2	650	O/W
Ludox TM50	Disperse in water and remains as drops in oil	7.0	520	O/W

Table 3: Identification of emulsion viscosity - emulsion type by drop test and conductivity measurements of oil [(olive, corn, soya bean and sunflower)-water, emulsion system] that stabilized by Ludox Sm 30.

Oil type	Drop test	Conductivity, µs	Emulsion type
Olive	Disperse in water and remains as drops in oil	980	O/W
Corn	Disperse in water and remains as drops in oil	550	O/W
Soya bean	Disperse in water and remains as drops in oil	490	O/W
sunflower	Disperse in water and remains as drops in oil	620	O/W

4. Conclusion

A nontraditional, edible and cheap surface active agent was used to prepare food emulsions of low adhesion power to polypropylene and polyester packaging films (plastic packaging materials). It was found that the best type of silica series (Nalco 1060, Ludox AM30, Ludox AS40, Ludox Sm30 and Ludox TM50) is Ludox Sm30. The amounts of adhered emulsion stabilized by Ludox Sm30 depend on the philicity of the packaging plastic sheet. The viscosity of the prepared emulsions of different oils has a significant effect on the adhesion of emulsion to packaging sheets. But, the philicity effect prevailed over the viscosity effect.

Acknowledgment:

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