Rheological investigation, Morphology and Time Dependent Stability of Water/Sun Flower Oil Emulsions

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Abstract:

In this this project, we have investigated the rheology of emulsion and effect of different parameters like homogenizing time, shearing time, stability, effect of volume fraction over rheology or stability etc. For the purpose, the emulsion was prepared by the emulsification of water in vegetable oil and the contents of water in emulsion were varied from 5-40% by volume. It has been noticed that the size was decreased and the number was increased with the increase in homogenizing time. The shear viscosity, storage modulus and loss modulus all the parameters were decreased with the increase in frequency of measurement, irrespective of water contents. The zero shear viscosity as well as the yield stress was increased with the

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volume fraction of water. The stability of the emulsion was decreased with the increase in water contents as the system became highly thermodynamically unstable.

Key words: Rheological investigation, Morphology, Time Dependent Stability, Water / Sun Flower Oil Emulsions

Introduction

The rheological characteristics of emulsions depend upon the rheological response of continuous media i.e. Newtonian and non-Newtonian, composition, droplets size and temperature etc [1]. On the other hand emulsions are transported, poured from one container to another and stored. During such processes the system experiences various shear stresses, shear rates, temperature variations or other such constraints [2-3]. These constraints significantly change the physical characteristics like stability, particle size distribution etc. of the emulsions. Though the increase in viscosity can stabilize the emulsion but it affects a lot its other important properties like flow/rheological characteristics. The literature reveal that there is no such studies carried out which can predict quantitatively the impact of shear stress/shear rates over the phase separation of emulsions [4].

Water-in-oil emulsions have variation in results with the passage of time which also affect the stability of the emulsions [5]. The important class of complex fluids prone to wall slip are dispersed systems, such as colloidal suspensions and emulsions, which adhere weakly or not at all to the shearing surfaces. In this case, slip is believed to arise from a depletion of particles adjacent to the shearing surfaces, resulting in local shear rates that can be much greater than that in the bulk fluid, i.e., an "apparent" 'wall slip [6]. This is particularly true for dense emulsions, where the viscosity is very sensitive to droplets

concentration. The apparent flow can markedly be different from that of the bulk, which has important implications with regard to both the rheological characterization and the processing of such materials. There have been a number of works reporting slip in dispersed systems; most often the presence of slip is inferred from rheological measurements only, rather than directly measured [7-12]. Relatively few studies have tried to correlate the rheology of slipping dispersions with direct flow observations. [13] Studied the wall slip of concentrated poly disperse emulsions simply by painting marker lines on the emulsions across the rheometer gap.

Viscosity of the emulsions is normally inversely proportional to the time, just at the formation of emulsions showing high viscosity and low coalescence rate, and variation present in loss and gain modulus [14]. It is worth noting that these flows have been observed in cone and plate geometries, where the shear stress is normally assumed to be constant [15-17]. Various microgel pastes and concentrated emulsions, flow-like yield stress fluids. Tracer particles and video microscopy are used to visualize the paste flow, with and without wall slip. A large number of foods items like cake, butter, margarine, mayonnaise, jellies, all drinks are examples of oil water emulsions and these can be in the form of solids or liquids [18-19]. Emulsions are also used in cosmetic, pharmacy, agriculture, oil rescue process and paints [20-25].

The free energy of the system increases during emulsification process and these are considered to be thermodynamically unstable and hence phase separation takes place with the passage of time [26]. Therefore, emulsification process requires huge amount of energy input. For this purpose, strong homogenizer, ultrasonification or vigorous stirring of the mixture is needed [27]. On the other hand different degree of stability is needed for various applications; therefore additives, particulates, viscous material to enhance the viscosity of the continuous media, surfactants, co-surfactants and/ or polymers

are added to control their stability [28-34]. In a stable emulsion, the interfacial area and free energy of the dispersion phase is decreased [35]. The time required to get the phases separated is considered as the stability of emulsion. The stability depends upon size, size distribution of drops, and viscosity of continuous media and over the dispersed phase, Different emulsion failure process can be represented by some of the instability of emulsion which produced layers separation in the emulsions, the sedimentation/creaming, aggregation or coalescence is the major factors which produce instability in the emulsion process [36-37]. In this study I have to determine the validity of the emulsions and yield stress which is very important for health aspects. And also show the morphology of the emulsions with volume fraction, droplets size droplets distribution, coalescence and stability of emulsions. Stability of the emulsion is directly depending upon droplets size and its distribution.

EXPERIMANTAL

Materials
In this study oils used was sunflower, obtained from the local market and was of high grade. Water used was double distilled and de-ionized and its conductance was maintained as 6-10μS.

Preparation of Emulsion
Keeping in view the importance of sunflower oil, it was used during this study. For the purpose, known amount of De-ionized water was added to oil and the mixture was homogenized at 500 rpm for 13 minutes using Ultraturix homogenizer, Germany. After preparing the emulsion, it was subjected to various studies. The same procedure of preparation was repeated for various oil/water compositions.

Viscosity Measurement

Brooke Field DV-E viscometer, Germany and Ostwald type capillary viscometers, were used for the determination of viscosity of emulsions prepared. A thermostatic bath was used for to keep the temperature constant.

Optical Microscopy

Just after the preparation of emulsion, it was subjected to optical microscopic measurement. For this purpose, an optical Swift M 4000-D microscope fitted with high performance computer controlled digital camera (CCD) was used. In this way, the number, size of droplets and their distribution was determined.

Rheological Measurements

To see the effect of shear forces over the emulsion, the rheology of emulsion was measured just after the preparation of emulsion using HAAK MARS11 advance modular Rheometer. The measurements were made using various shear rates and oscillating frequency.

RESULTS & DISCUSSIONS

Emulsification

The phenomenon of emulsification as well as de-emulsification/coalescence process is very important and complicated one. On one side the industries need specified stability of emulsion and on other hand separation of oil from water is very much needed for economics/environmental purpose. Therefore it is need of the day to understand the process in detail. Keeping in view these facts we have investigated both the process up to large extant and the outcome is discussed over here.

Effect of Volume Fraction

The water/oil system was emulsified using strong homogenizer and mixing the system at 500rpm for 15 minutes. Some of the micrographs of water in oil emulsification obtained in this way are displayed in Fig 1. The size distribution for each volume percent has been displayed in the form of histograms (Fig 2-9). These histograms indicated that the wideness of size distribution first decrease and then increases with the increase in volume percent of water and it is minima for 10 % water in oil.(38) These histograms also indicated that by increasing the volume fraction of water the instability increases and hence the equilibrium is shifted towards coalescence. The numeral values regarding number of droplets, size and clusters are listed in Table 1. The same data has also been displayed in Fig 10, while their size distribution in Fig 11(39). These figures indicated that the size was largest when the water volume percent was 25 in water-in-oil emulsion while number was highest for 15%.
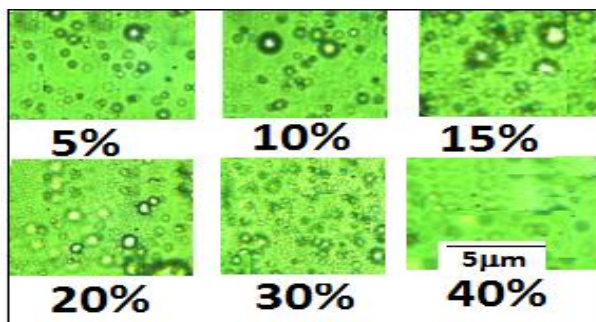
Fig. 1:   Micrographs of the water/oil emulsion having different water contents and homogenized for 15 minutes
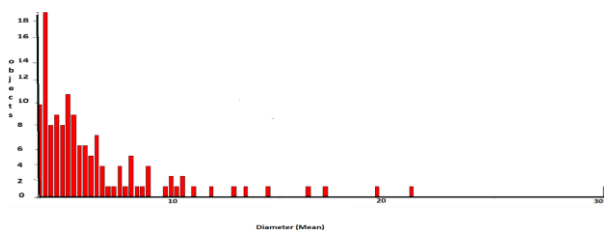
Fig. 2: Mean diameter of emulsion droplets having 5% water-in-oil
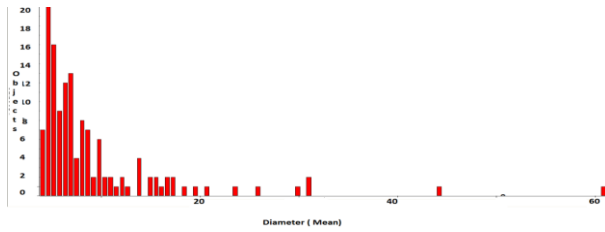
Fig. 3: Mean diameter of emulsion droplets having 10% water-in-oil
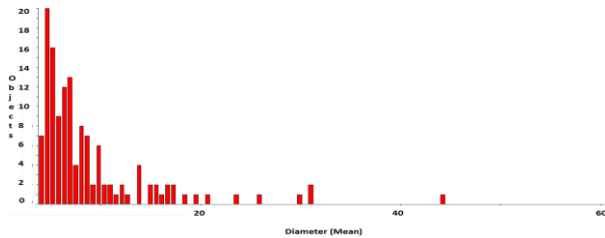
Fig. 4: Mean diameter of emulsion droplets having 15% water-in-oil
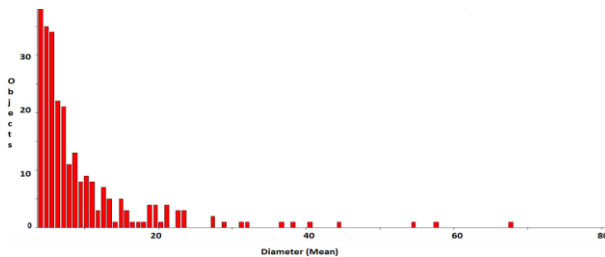
Fig. 5: Mean diameter of emulsion droplets having 20% water-in-oil
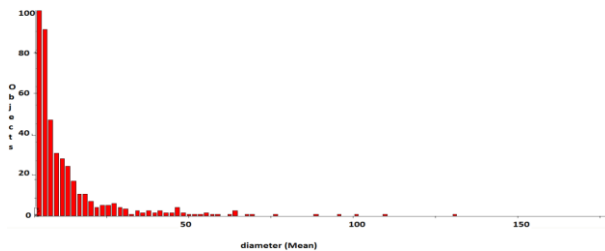
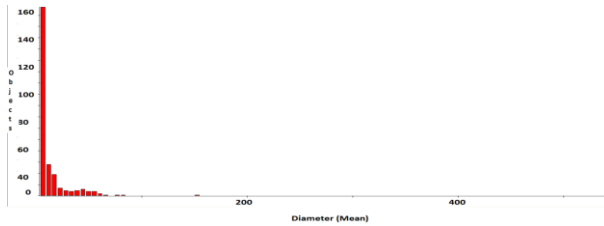**Fig. 6: Mean diameter of emulsion droplets having 25% water-in-oil**

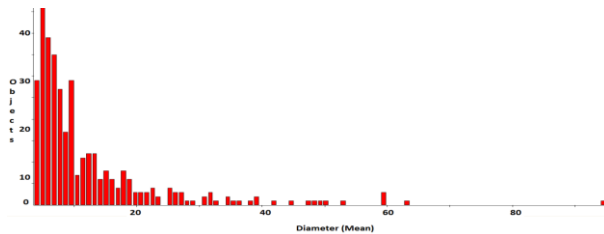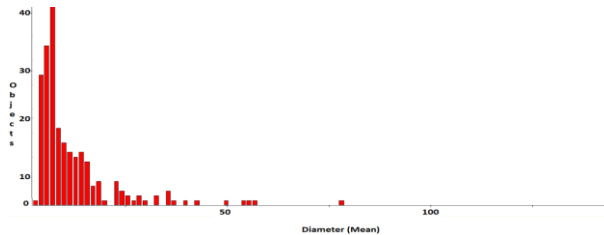**Fig. 7:   Mean diameter of emulsion droplets having 30% water-in-oil**

Fig. 8: Mean diameter of emulsion droplets having 35% water-in-oil

Fig. 9:   Mean diameter of emulsion droplets having 40% water-in-oil

Table 1: Various parameters of emulsions obtained from micrographs

Volume Fraction	Class	Objects	% Objects	Mean Diameter (max)	Mean Diameter (min)	Mean Diameter (mea)
5	Clusters	228	47.01	6.88	3.50	5.27
	Single	257	52.98	1.26	1	1.13
10	Clusters	225	38.07	8.85	4.44	6.58
	Single	366	61.92	1.23	1	1.11
15	Clusters	1882	65.09	12.32	5.47	8.77
	Single	1009	34.90	2.10	1.25	1.68
20	Clusters	332	68.73	11.58	5.41	8.52
	Single	151	31.26	1.84	1.14	1.49
25	Clusters	621	70.40	16.98	7.32	11.76
	Single	261	29.59	1.53	1.02	1.28
30	Clusters	318	61.74	16.25	9.89	13.01

	Single	197	38.25	1.49	1.03	1.26
35	Clusters	422	71.40	15.35	6.54	10.80
	Single	169	28.59	1.49	1.02	1.26
40	Clusters	260	64.84	14.58	7.38	10.88
	Single	141	35.16	1.26	1	1.34
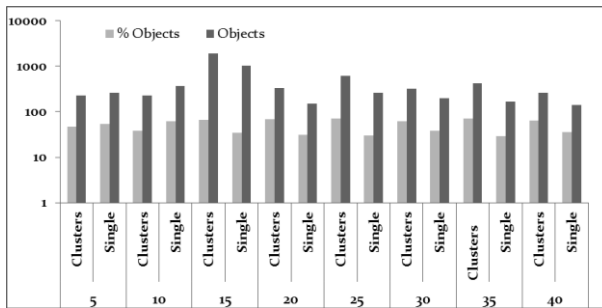
Fig. 10: Number of single droplets and their clusters as a function of volume percent of water
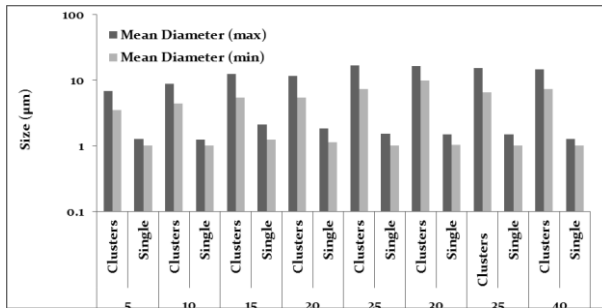
Fig. 11: Size of single droplets and their clusters as a function of volume percent of water

Effect of Shearing Frequency

The emulsion prepared by homogenizing the oil water mixture containing 5% water was subjected to dynamic Rheometer after different time intervals. The results obtained for complex viscosity, storage and loss modulus are recorded in Figures 12-43. It can be noted that the viscosity decrease with shearing time whereas both the modulus remain constant. However, the initial viscosity as well as the change in viscosity with reference

to shear time increases with the coalescence time. This trend increase that as the time passes the coalescence process increases and the drops are increased, resulting high viscosity. The same process was carried out for other volume fractions till 40%.(40-41)The same trend was observed except that the dispersion in data was increased with the increase in volume fraction indicating that either the emulsion was not properly formed or instability in the system was increased with the increase in volume fraction. If we observed the earlier discussed data the micrographs it can be concluded that though the emulsion prepared in case of high volume fraction was not perfect but the contribution of coalescence process was significant. The viscosity variations and initial viscosity data has also been plotted in Fig 44. This figure indicates that as volume fraction of oil in the emulsions systems was decreased the rate of coalescence was increased and the stability of the systems was decreased. (42)

Effect of Time Period

The rheological measurements were also performed after different time period of coalescence process. It can be noted that with the passage of time, coalescence rate increases and the stability of the system was decreased Fig 44. Further the data obtained for 10% emulsion indicated fewer rates of coalescence and high degree of stability than 20% emulsion, and so on. We see that the viscosity of samples varied as 5<10<15<20<25<30<35<40 variations were low for high volume fraction, concluding that the coalescence process was (5>10>15>20>25>30>35>40) decreased with the increase in volume fraction.(43)
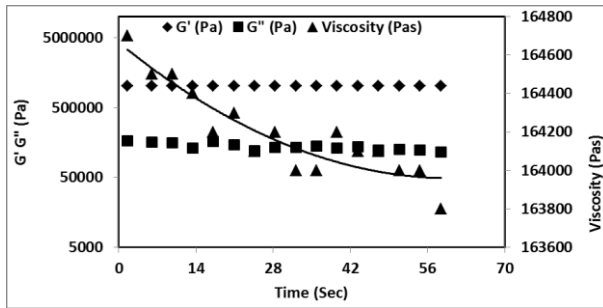
Fig 12: Storage modulus, loss modulus and viscosity of emulsion having 5% water in oil as a function of shearing time
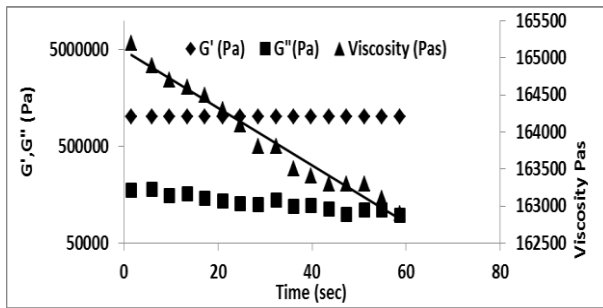

Fig 13: Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 5% after 5 minutes of formation of emulsion
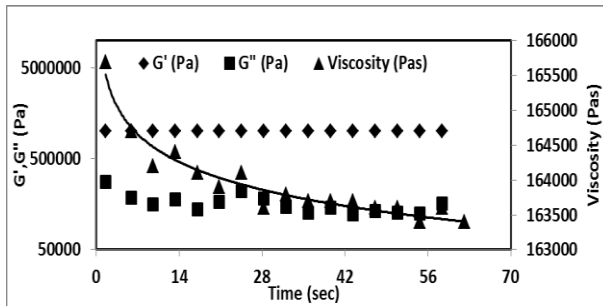

Fig 14 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 5% after 10 minutes of formation of emulsion
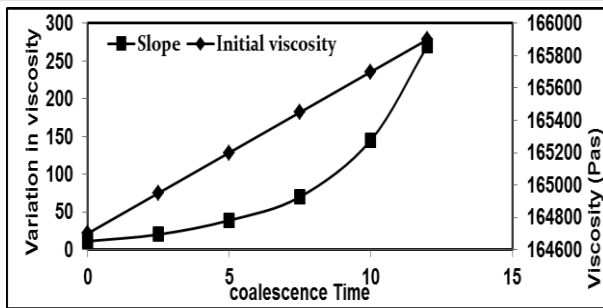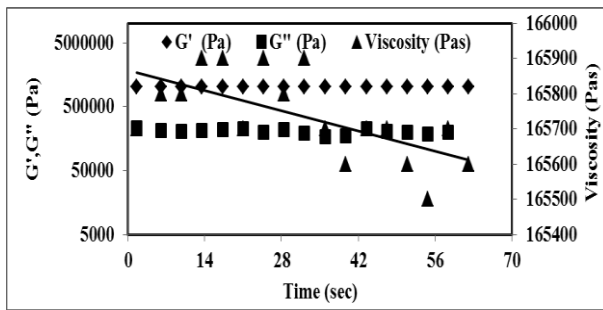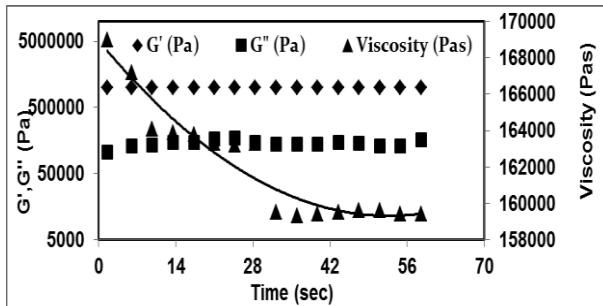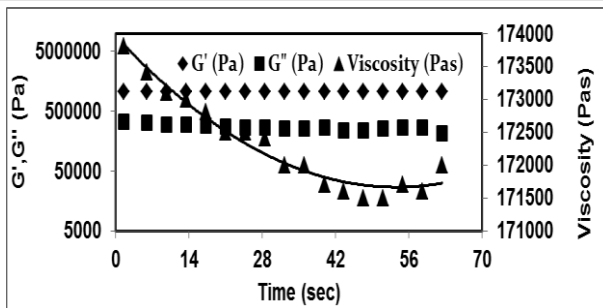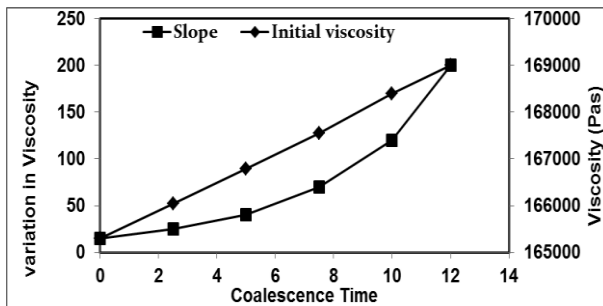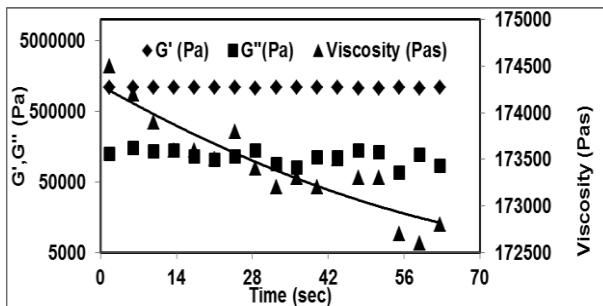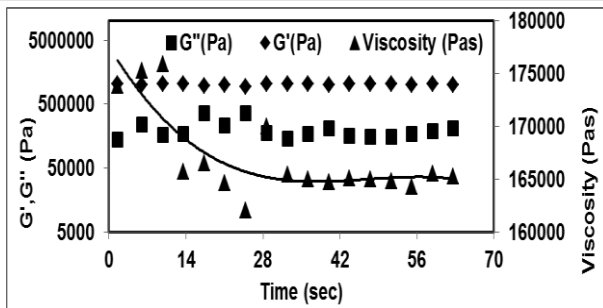
Fig 15   Rate of coalescences 5% (W/O) emulsion

Fig 16: Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 10% just after the formation emulsion

Fig 17 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 10% after 5 minutes of formation of emulsion
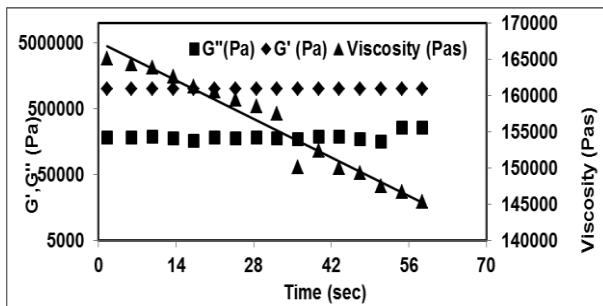
Fig 18 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 10% after 10 minutes of formation of emulsion
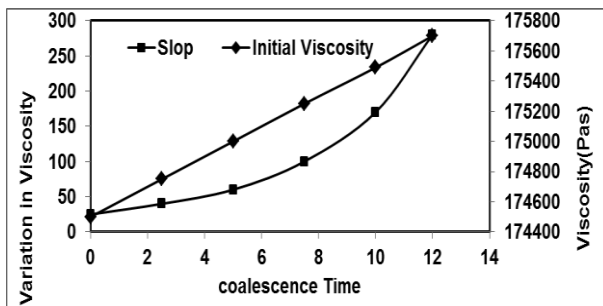

Fig 19   Rate of coalescences of 10% W/O emulsion

Fig 20: Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 15% just after the formation of emulsion

Fig 21: Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 15% after 5 minutes of formation of emulsion

Fig 22 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 15% after 10 minutes of formation of emulsion

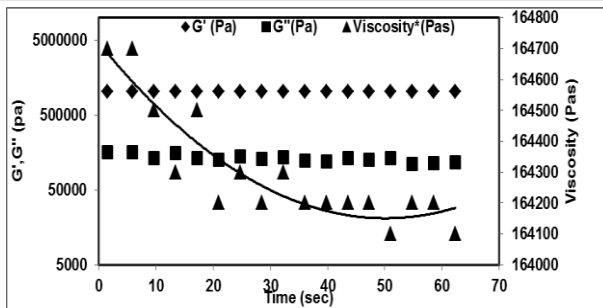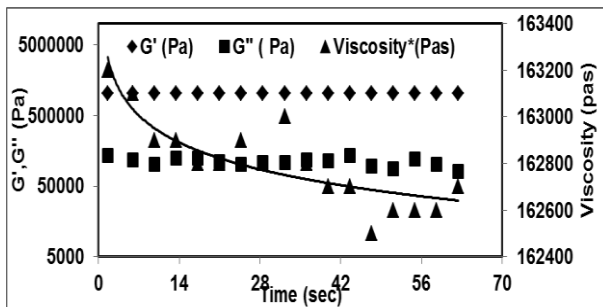
Fig 23 Rate of coalescence 15% (W/O) emulsion

**Fig 24 Storage modulus, loss modulus and viscosity as a function of
shearing time curve having emulsion 20% just after the formation of
emulsion**

**Fig 25: Storage modulus, loss modulus and viscosity as a function of
shearing time curve having emulsion 20% after 5 minutes of
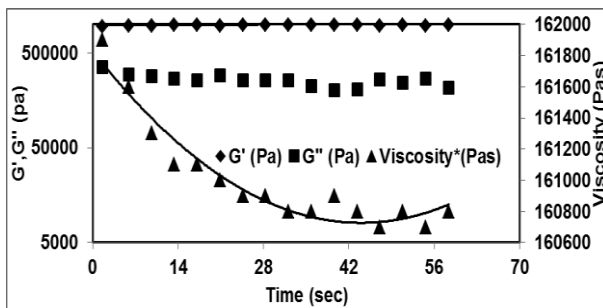formation of emulsion**

**Fig 26 Storage modulus, loss modulus and viscosity as a function of
shearing time curve having emulsion 20% after 10 minutes of
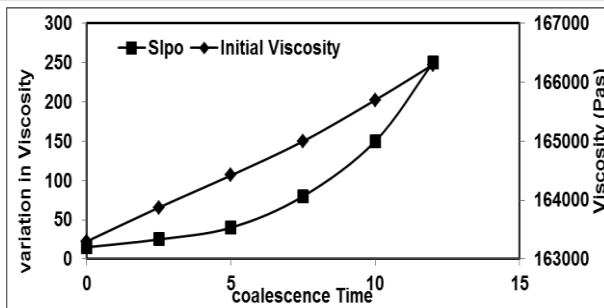formation of emulsion.**
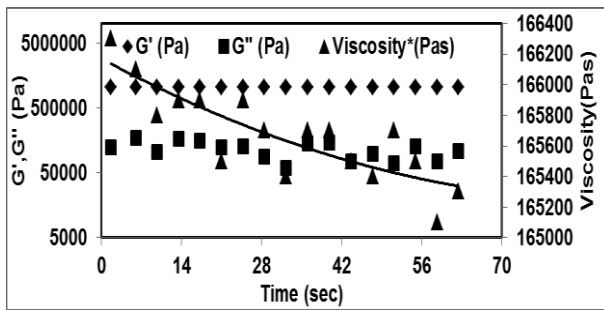
Fig 27   Rate of coalescence 20% (W/O) emulsion

Fig 28: Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 25% just after the formation of emulsion
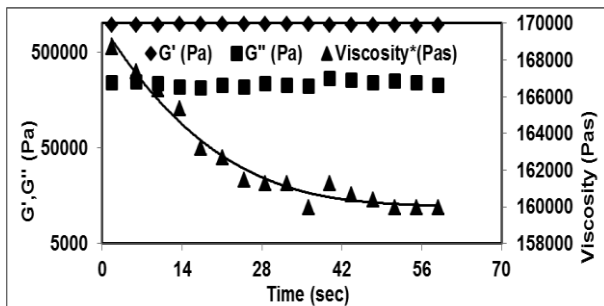

Fig 29   Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 25% after 5 minutes of formation of emulsion
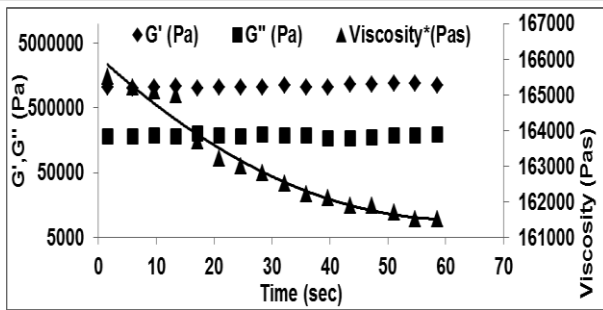
Fig 30 **Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 25% after 10 minutes of formation of emulsion**

Fig 31 **Rate of coalescence 25% (W/O) emulsion**

Fig 32 **Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 30% just after the formation of emulsion**

Fig 33   Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 30% after 5 minutes of formation of emulsion

Fig 34   Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 30% after 10 minutes of formation of emulsion
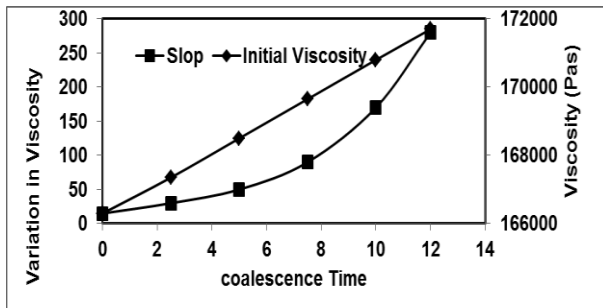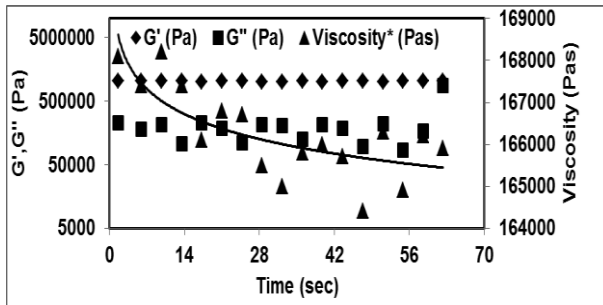

Fig 35   Rate of coalescence 30% (W/O) emulsion
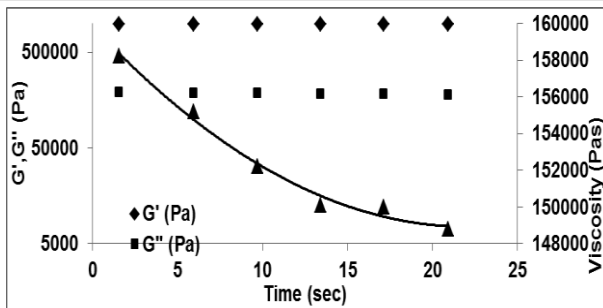
Fig 36 Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 35% just after the formation of emulsion
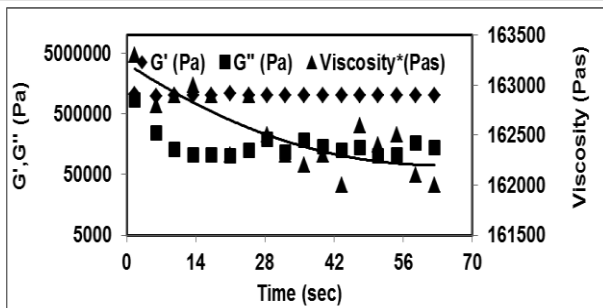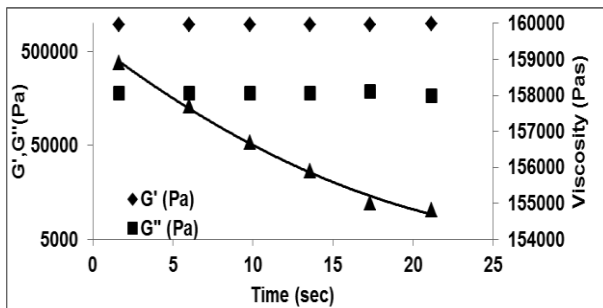

Fig 37 Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 35% after 5 minutes of formation of emulsion
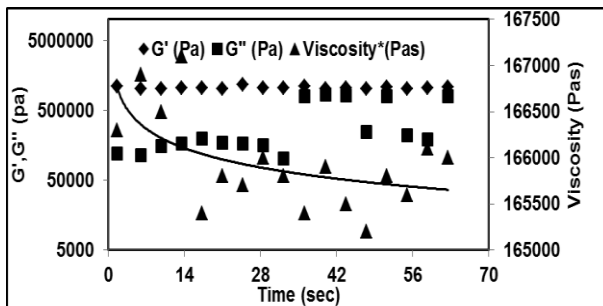

Fig 38 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 35% after 10 minutes of formation of emulsion

Fig 39   Rate of coalescence 35% (W/O) emulsion

Fig 40   Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 40% just after the formation of emulsion

Fig 41 Storage modulus loss modulus and viscosity as a function of shearing time curve having emulsion 40% after 5 minutes of formation of emulsion
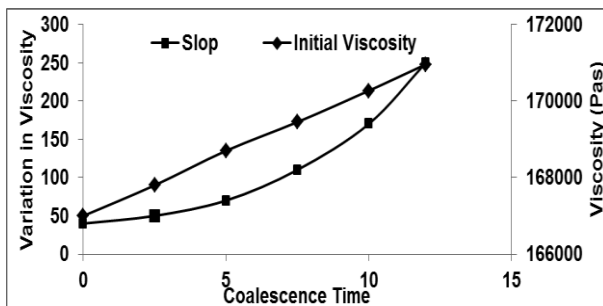
Fig42 Storage modulus, loss modulus and viscosity as a function of shearing time curve having emulsion 40% after 10 minutes of formation of emulsion

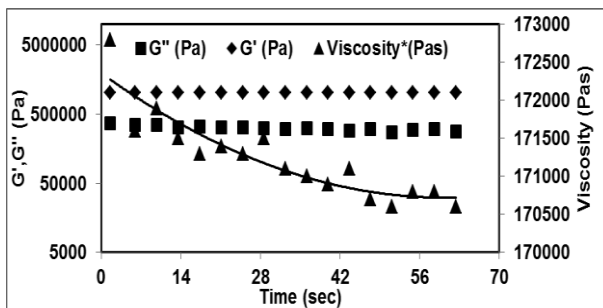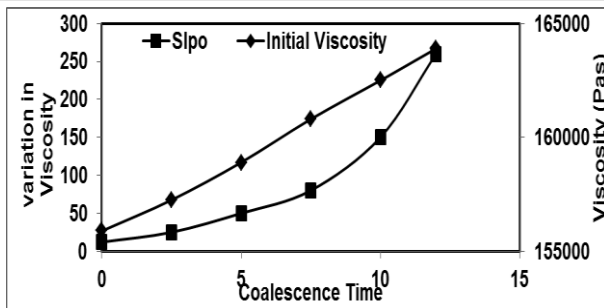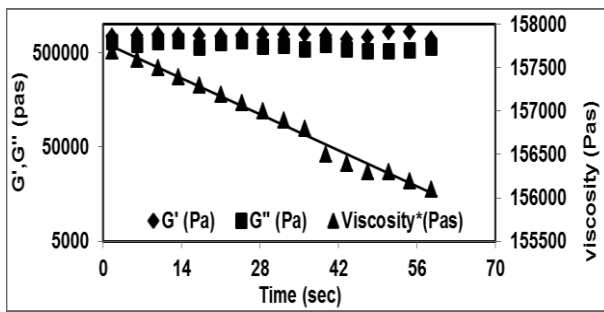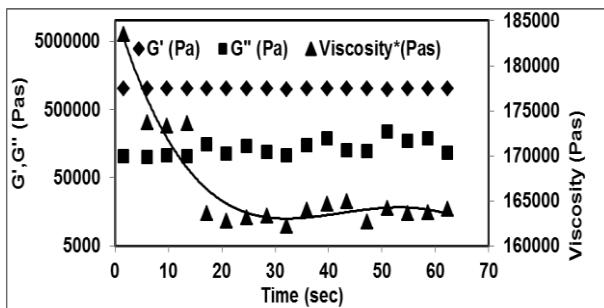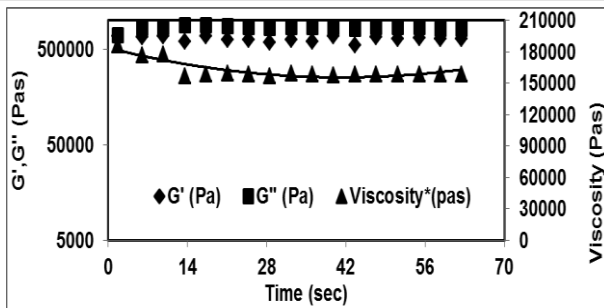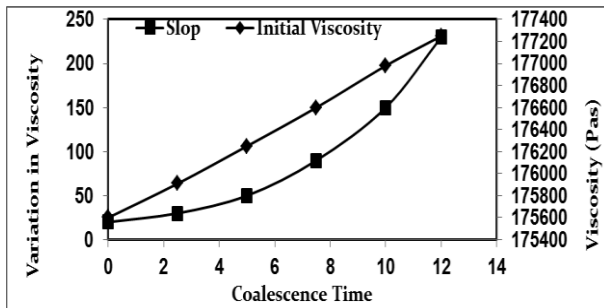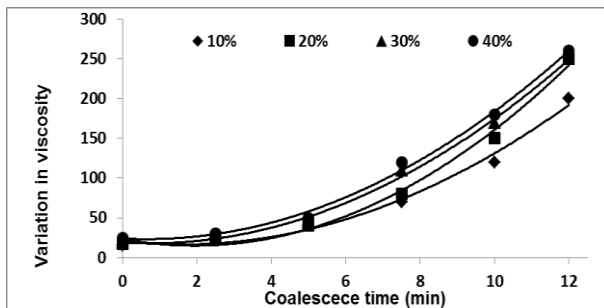**Fig 43 Rate of coalescence 40% (W/O) emulsion**

Fig 44 Rate of coalescence having 10%, 20%, 30%, and 40% water-in-oil emulsions

CONCLUSION

Emulsification of oil-water system has been investigated over a wide (5-40%) range of volume fraction of water. It has been concluded that as the volume fraction increases, the degree of dispersity was increased. The stability was also noted to be decreased with the increase in volume fraction of water. The complex viscosity, storage and loss modulus were function of water contents in emulsion. The rate of coalescence was function of time volume fraction and time. It was quite high for high volume fraction and remained high up to sufficiently long time. It was concluded that the rate of coalescence was increased with the increase in volume fraction of water. The shearing of emulsion over different time intervals concluded that the stability against the shear forces decreases with the passage of time. The shearing of emulsion as a function of oscillating frequency, volume fraction of water and the passage of time concluded that the coalescence process is a highly complicated system and depends upon the size, number of droplets and their distribution in addition to volume fraction, oscillating frequency and shear rate.

Emulsions are considered to be very important fluids due to their specific characteristic and application in medicine, petroleum, cosmetics, chemicals and food industries. The work reported up to now is mostly on complicated systems consisting of water, oils, electrolytes, surfactants and several other such materials. However it does not provide the insight story of the process. Therefore our objective was to find out the exact mechanism of emulsification and see the role of different parameters over its quality and stability etc. For emulsification process water is emulsified in vegetable oil (Sun flower oil), considering it as a model for food emulsion. The role of oil contents, and shear forces upon emulsification and Rheological behavior have been investigated using Rheometer. The main objective of this work was to show, these interactions enter the

modeling of Rheometric functions particularly, and shear viscosity.

REFERENCES

1. Barnes, H. A.,"A review of the slip ~wall depletion! of polymer solutions, emulsions and particle suspensions in viscometers: its cause, character, and cure," J. Non-Newtonian Fluid Mech. 56, 221–251 ~1995!.

2. Buscall, R., J. I. McGowan, and A. J. Mortonjones,"The rheology of concentrated dispersions of weakly attracting colloidal particles with and without wall slip," J. Rheol. 37, 621–641 ~1993!

3. Plucinski, J., R. K. Gupta, and S. Chakrabarti, "Wall slip of mayonnaises in viscometers," Rheol. Acta 37, 256–269 ~1998!

4. Pal, R., "Slippage during the flow of emulsions in rheometers," Colloids Surf., A 162, 55–66 ~2000!.

5. Russell, W. B., and M. C. Grant, "Distinguishing between dynamic yielding and wall slip in a weakly flocculated colloidal dispersion," Colloids Surf., A 161, 271–282 ~2000!.

6. Walls, H. J., S. B. Caines, A. M. Sanchez, and S. A. Khan, "Yield stress and wall slip phenomena in colloidal silica gels," J. Rheol. 47, 847–867 ~2003!.

7. Meeten, G. H., "Squeeze flow of soft spheres between rough surfaces," Rheol. Acta 43, 6–16 ~2004!.

8. Princen, H. M., "Rheology of foams and highly concentrated emulsions. II. Experimental study of the yield Stress and wall effects for concentrated oil-in-water emulsions," J. Colloid Interface Sci. 105, 150–171~1985!.

9. Aral, B. K., and D. M. Kalyon, "Effects of temperature and surface roughness on time-dependent development of

wall slip in steady torsional flow of concentrated suspensions," J. Rheol. 38, 957–972 ~1994!.

10. Salmon, J.-B., L. Be´cu, S. Manneville, and A. Colin, "Towards local rheology of emulsions under couette flow using dynamic light scattering," Eur. Phys. J. E 10, 209–221 ~2003!.

11. Pignon, F., A. Magnin, and J.-M. Piau, "Thixotropic colloidal suspensions and flow curves with minimum: Identification of flow regimes and rheometric consequences," J. Rheol. 40, 573–587 ~1996!.

12. Coussot, P., J. S. Raynaud, P. Moucheront, J. P. Guilbaud, H. T. Huynh, S. Jarny, and D. Lesueur, "Coexistence of liquid and solid phases in flowing soft-glassy materials," Phys. Rev. Lett. 88, 218301/1–4 ~2002b!.

13. Varnik, F., L. Boquet, J.-L. Barrat, and L. Berthier, "Shear localization in a model glass," Phys. Rev. Lett. 90, 095702/1–4 ~2003!.

14. Picard, G., A. Ajdari, L. Bocquet, and F. Lequeux, "A simple model for heterogeneous flows of yield stress fluids," Phys. Rev. E 66, 051501/1–12 ~2002!.

15. B. R. Raonizafinimanana, E. M. Gaydou and I. Bombarda, *J. Agric. Food Chem.*, **1997**, *45*, 2542–2545.

16. E. Rudnik, A. Szczucinska, H. Gwardiak, A. Szulc and A. Winiarska, Therochemica Acta, 2001, 370, 135-140.

17. C. Golumbic, H. A. Mattill, *J. Am. Chem. Soc.*, **1941**, *63*, 1279–1280.

18. A. M. Marina, Y.B. Che Man and I. Amin, Trends in Food Science and Technology, 2009, 20, 481-487.

19. Th. Dimming, J. Haupt and W. Radig, Freiberger. Forschungshefte. A, 1999, 852, 34- 60.

20. G. A. Reinhardt and S. O. Gartner, 4th International Colloquium on Fuels 2003, Technische Akademie

Esslingen, Ostfildern (Germany), 15-16 January 2003., 111-114.

21. J. Krahl, A. Munack, O. Schroder, H. Stein, M. Dutz and J. Bunger, 4th International Colloquium on Fuels 2003, Technische Akademie Esslingen, Ostfildern (Germany), 15-16 January 2003, 115-123.

22. J. Hancsok, and F. Kovacs, The Biodiesel. Essay, BME OMIKK Environmental Papers, Budapest, January, 2002, 56.

23. A. Kumar and S. Sharma, Industrial Crops and Products, 2008, 28, 1-10.

24. Y. Yilmaz, Trends in Food science and Technology, 2006, 17, 64-71.

25. A. Esmailzadeh and L. Azadbakht, Am. J. Clin. Nutr., 2008, 88, 913-921.

26. R. J. Singh, and T. Himowitz, *Genome*, 1999, 42, 605-616.

27. G. R. Dixon, J. Plant Growth Regul., 2009, 28, 194-202.

28. Y. Wang, S. Ou, P. Liu and Z. Zhang, Energy Conversion and Management, 2007, 48, 184-188.

29. H. Schwartz, V. Ollilainen, V. Piironen and A. M. Lampi, Journal of Food Composition and Analysis, 2008, 21, 152-161.

30. R. A Moreau, B. D. Whitaker and K. B. Hicks, Progress in Lipid Research, 2002, 41, 457–500.

31. R.O. Dunn, J. Am. Oil. Chem. Soc., 1999, 76, 109–115.

32. D. P. Geller and J. W. Good rum, J. Am. Oil. Chem. Soc. 2000, 77, 111–114.

33. H. A. Barnes, Barnes. (1994); "Rheology of emulsions - a review", Colloids Surf. A, 91, 89-95.

34. T. F. Tadros. (1994); Fundamental principles of emulsion rheology and their applications, Colloids Surf A, 91, 39-55

35. R. Pal, Y. Yan, and J. Masliyah, (1992); Schramm L.L.Editor Advances in Chemistry Series-231: Washington DC, Chapter-4.

36. A.A. Peña, G.J. Hirasaki, and C.A. Miller, (2006); Adv. Colloid Interface Sci., 123–126,241–257.

37. J. Weiss, C. Canceliere, and D.J. McClements (2000); Ostwald Ripening", Langmuir, Vol. 16, No. 17.

38. Liu, H., Xu, X.M., Guo, S.D., 2007. Rheological, texture and sensory properties of low-fat mayonnaise with different fat mimetics. Lebensm Wiss Technol. 40, 946-954.

39. Worrasinchai, S., Suphantharika, M., Pinjai, S., Jamnong, P., 2006. -Glucan prepared from spent brewer's yeast as a fat replacer in mayonnaise. Food Hydrocolloid. 20, 60-78.

40. Hayati, I.N., Man, Y.B.C., Tan, C.P., Aini, I.N., 2007. Stability and rheology of concentrated O/W emulsions based on soybean oil/palm kernel olein blends. Food Res. Int. 40, 1051–1061.

41. Princen, H. M., "Rheology of foams and highly concentrated emulsions. III: Static shear modulus," J. Colloid Interface Sci. **112**, 427–437 ~1986