RHEOLOGICAL CONSISTENCY OF CONCENTRATED WATER-IN-OIL EMULSION

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Abstract

We have studied a relationship between the pattern of complex modulus change versus internal phase volume ratio and the rheological consistency of concentrated W/O emulsions with Magnesium Sulfate in the range 0.0 to 0.5 wt% and with different oil polarities, respectively.

The rheological consistency with time of concentrated W/O emulsion was checked using Fudoh Rheometer and the coalescence of deformed water droplets was examined using polarized light microscope(LEICA DMRP). To find the pattern of complex modulus change of the concentrated emulsions versus internal phase volume ratio, the effect of varying water phase volume fraction from 0.78 up to 0.85 on viscoelastic measurements was investigated using rotational rheometer (HAAKE RheoStress RS 50).

The rheological consistency was mainly destroyed by the coalescence of the deformed water droplets. The greater the increase of complex modulus was, the less coalescence occurred and the more consistent the concentrated emulsions were. And the pattern of complex modulus increase versus volume ratio has been explained with the resistance to coalescence of the deformed interfacial film of water droplets in concentrated W/O emulsion.

Introduction

Concentrated emulsions have an internal phase that occupies more than 74% of the available volume. And there exists a maximum amount of internal phase that can be incorporated into concentrated emulsion. The maximum volume ratio of dispersed phase is where rheological properties such as zero shear viscosity or complex modulus of concentrated W/O emulsions (with volume ratio of water phase greater than 0.74) dramatically increase. The ratio between this maximum amount and the amount of continuous phase depends upon the nature of emulsifiers, the polarity of oils, the concentration of electrolyte and etc.

Also this maximum amount depends upon the conditions under which these emulsions are prepared, such as power of mixing or mixing time. So it is really difficult to determine this maximum amount critically. And there is little doubt today that water-continuous or oil-continuous emulsions approaching 100% internal phase volume can be prepared.

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In this paper the effect of varying the water phase volume ratio on viscoelastic measurements was examined. With increasing water phase volume ratio, the complex modulus of the emulsion increased. The pattern of complex modulus increase with increasing water phase volume ratio was investigated rather than maximum amount of internal phase was. And we observed that the pattern of complex modulus increase is closely related to the consistency of W/O concentrated emulsions. And the relation could be explained with the resistance to coalescence of the deformed interfacial film of water droplets in concentrated W/O emulsion.

Experimental

Materials

Cetyl Dimethicone Copolyol (Abil EM 90) was commercial grade obtained from Goldschmidt. Cyclomethicone (Silicone oil) was from Dow Corning, Natural Squalane from Kishimoto (Japan) and Octyl Dodecanol (Eutanol G) was from Henkel (Germany). Glycerin was from LG Chemicals (Korea) and Magnesium Sulfate ($MgSO_4$) was from Wonjin Chemicals (Korea). Water was de-ionized using Milli RO 12 plus from MilliPore.

Procedures

The W/O concentrated emulsions were prepared to investigate the relationship between rheological consistency of emulsions and the pattern of complex modulus increase with increasing internal phase volume. We were to verify this relationship for two groups respectively. The group named E is a set of samples to incorporate electrolyte into emulsions. The group named P is a set of samples to vary the polarity of outer phase, oils. The formulations are as follows;

Table 1. Formulations for measuring rigidity

Name of sample	Group E			Group P		
	E1-2	E2-2	E3-2	P1-2	P2-2	P3-2
Squalane	4.0	4.0	4.0	4.0	2.0	-
Eutanol G	-	-	-	-	2.0	4.0
Silicone oil	13.0	13.0	13.0	13.0	13.0	13.0
Abil EM 90	2.0	2.0	2.0	2.0	2.0	2.0
D.I Water	to 100	to 100	to 100	to 100	to 100	to 100
Glycerine	5.0	5.0	5.0	5.0	5.0	5.0
MgSO4	-	0.3	0.5	-	-	-

Then, the rigidity of above 6 samples kept in 25 chamber was measured using Fudoh rheometer to check the rheological consistency of emulsions for 2 months. And the coalescence of deformed water droplets was examined using polarized microscope.

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And to measure the pattern of complex modulus increase with increasing internal phase volume, we made emulsions having different internal volume ratio for each sample. For example, in case of sample E1-2, then we made two other samples having internal volume ratio 0.78 and 0.85 respectively. Then the sample having internal volume ratio 0.78 was named E1-1 and the sample with 0.85 was E1-3. The last number following hyphen (-) was used to indicate internal volume ratio such as -1 for 0.78, -2 for 0.81 and -3 for 0.85 respectively.

Oscillation test was carried out on all samples to measure complex modulus and loss angle() using RheoStress RS 50 from HAAKE. Temperature is controlled 25.00.2 by Peltier Plate Temperature Controller base (Model TC80). We used 35mm cone with angle 1. From these results, the pattern of complex modulus change versus internal volume ratio was checked.

Results and Discussion

For Group named. E , the results for rheological consistency show that sample with 0.3wt% $MgSO_4$(sample E2-2) is the most consistent with time among three samples. See Table 1 and Fig.1. And the results for the pattern of complex modulus increase show that sample with no $MgSO_4$ is the steepest in slope. And the sample with 0.3wt% MgSO4 shows the lowest increase. See Table 2 and Fig.3..
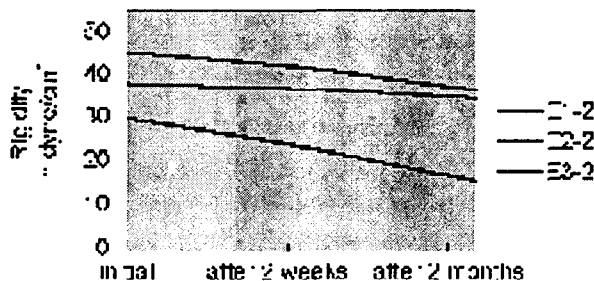

Fig 1 Rigidity Change of Group E with time

For Group named. P , the results for rheological consistency show that sample P2-2 and sample P3-2 show similar consistency with time and sample P1-2 shows the largest decrease in rigidity among three samples. See Table 1. And the results for the pattern of complex modulus increase show that sample P2-series and sample P3-series show similar pattern of complex modulus increase and sample P1-series shows the largest increase. See Table 2 and Fig.4.

The results for the pattern of complex modulus increase can be explained as follows. As the water phase volume increases, the solvate shell is more reduced or interfacial layers are more compressed. And the rheological response can be seen as increase of the complex modulus(Fig.2). To guarantee a high emulsion stability against coalescence, interfacial layer should be very stable. If not so, interfacial layer would be broken down and consequently water droplets would be coalesced.
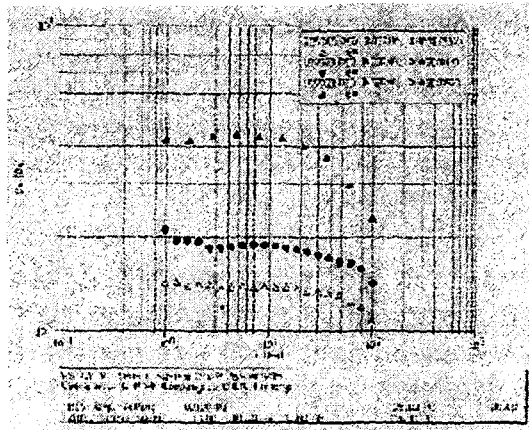
Fig.2   Rheogram of Oscillation test for E2 series

(Filled triangle stands for E2-1, filled circle stands for E2-2, and open triangle stands for E2-3)
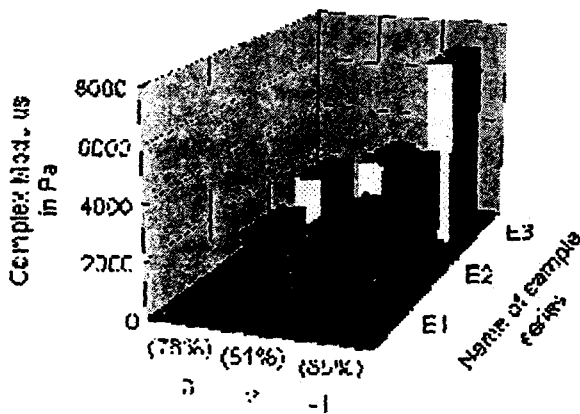

Fig.3   Complex Modulus Change of Group E versus Water Phase Volume Ratio
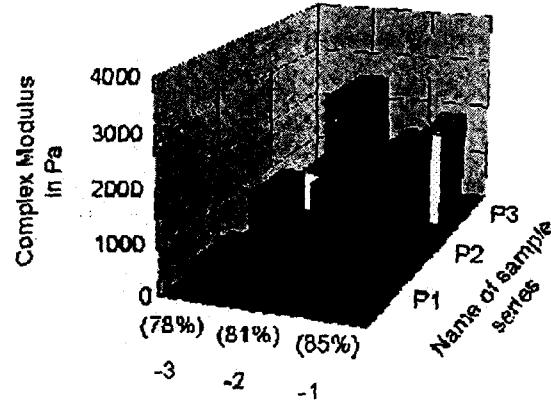

Fig.4   Complex Modulus Change of Group P versus Water Phase Volume Ratio

So it can be said from the results of rheological consistency that in case of W/O concentrated emulsions the less coalescence occurred, the more stable the interfacial layer is. And the results show that the greater the increase of complex modulus was, the less coalescence occurred and the more consistent the concentrated emulsions were.

Thus the pattern of complex modulus increase versus internal phase volume ratio could be measured to relatively predict an ability of water droplets in W/O concentrated emulsions to resist to coalescence. That is, if there is a exponential increase in complex modulus with increasing water phase volume ratio, it could be expected that the rheological consistency might not be so good.

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Table 2. Rigidity change with time(Rigidity in dyne/cm^2)

Sample name	Group 1			Group 2		
	E1-2	E2-2	E3-2	P1-2	P2-2	P3-2
initial	.29	.38	.45	.29	.24	.26
after 2 weeks	.23	.37	.42	.23	.22	.23
after 2 months	.16	.35	.37	.16	.17	.18

Table 3. Increase of Complex Modulus with Increasing Water Phase Volume Ratio (Complex Modulus in Pa)

Sample name (Water Phase volume ratio)	Group 1			Group 2		
	E1	E2	E3	P1	P2	P3
-1 (85%)	3800	4100	7100	3800	2200	1900
-2 (81%)	900	1900	2900	900	1400	1100
-3 (78%)	600	1300	2000	600	1100	800

Conclusion

The rigidity of W/O concentrated emulsion decreased with time. The decrease is mainly caused by the coalescence of water droplets and it can be seen using polarized light microscope. For each group, the smaller the amount of complex modulus increase was, the less coalescence occurred and consequently the more consistent the concentrated emulsion was. From these results, it can be concluded that the pattern of complex modulus increase versus internal phase volume ratio could be used as an index to relatively predict the rheological consistency of W/O concentrated emulsions.

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