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Emulsions containing vegetable oils for cutting fluid application

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Abstract

Emulsions of vegetable oils were prepared using ionic and non-ionic surfactants for use as metal working fluids. The conditions for an enhanced mutual miscibility for soybean oil or modified soybean oil and water were investigated to prepare emulsions for vegetable oil-based components. Oil modification was achieved using ozonation and sulfurization reactions. The products were characterized using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The viscosities of the modified oil were considerably higher than the starting oil. The emulsions were obtained with the aid of three different surface-active agents at room temperature. The stability and efficiency of these emulsions were evaluated. These emulsions also showed good stability and anticorrosion properties. The phase behavior was evaluated using phase diagrams. Cryo-scanning electron microscopy (cryo-SEM) was used in describing the oil–water interaction during the emulsion formation. It was found that the phase behavior was dependent on the nature and the concentration of surfactant used. Modified soybean oil required comparatively increased amounts of surfactant than the regular oil to obtain a stable emulsion.

Keywords: Metalworking fluids; Vegetable oils; FTIR; NMR; Cryo-SEM

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1. Introduction

Oils and fats are water-insoluble substances derived from vegetable and animal sources. Over the years, oils and fats have been used and retained their importance as metalworking lubricants. However, due to the complexity and special requirements of the new age metalworking fluids, such as extreme pressure and corrosion resistance, these oils and fats need to be modified or compounded. The predominance of the mixed-film lubrication mechanism demands that boundary and extreme pressure lubricants be added to oils possessing viscous properties. Thus, almost all lubricants require further additives to impart other characteristics of a non-tribological nature, such as oxidation resistance, corrosion protection, and detergency. Most metalworking lubricants, vegetable-based and petroleum-based, are compounded or modified to achieve these requirements. Several methods are available to modify these oil lubricants. The important and most commonly used methods are sulfurization and phosphate modification [1,2].

The growing demand for biodegradable materials has opened an avenue for using vegetable oils as an alternative to petroleum-based polymeric materials [3,4]. Soy-based products constitute a major portion of US agricultural products. Soybean oil, widely used as a food material, has the potential to be used as a renewable resource in place of petroleum-based materials [5]. Major disadvantages of vegetable oils are inadequate oxidative stability and problems associated with use in high or low temperature applications [6,7]. The poor oxidative stability is typically due to the rapid reactions occurring at the double bond in the oil molecule. Reactions like free radical oxidation, hydrogen abstraction, addition reaction, fragmentation, rearrangement, disproportionation reaction, and polymerization can reduce oxidative stability. These problems can be mitigated by the structural modification of vegetable oil by chemical reactions [8]. Research conducted in our laboratory has shown that soy flour and soybean oil can replace petroleum-based polymer and polyurethane materials [9,10]. To alleviate the problem of oxidative instability, ozone and sulphur modification were also conducted in our laboratory. Vegetable oil-based emulsions were also a part of recent research to produce stable emulsions to use as metalworking fluids and in other applications [11–13]. Most attention has been given to veg-

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etable oil-based emulsions, and few references are available on these emulsions as metalworking fluids. In the present study, we investigated vegetable oil emulsions containing modified and unmodified soybean oil. The use of vegetable oil in metalworking applications may alleviate problems faced by workers, such as skin cancer and inhalation of toxic mists in the work environments. This will also help to add value to a farm commodity, such as soy oil and other similar vegetable-based oils. This study deals with the development of a vegetable-based emulsion that can be used in the metalworking industry to replace partially or completely the commonly used petroleum-based emulsions. Vegetable oils have good lubricating ability and have been used for the formulation of rolling emulsions. However, certain limitations prevent their wide use in lubrication applications. They are easily hydrolyzed, and a thin layer is often formed on finished products. The objective of this study was formulation of vegetable oil emulsions, to replace synthetic esters commonly used as metalworking fluids.

This paper describes a method for the formulation of vegetable oil-in-water emulsions. These emulsions were prepared using various surfactants, and the stability of these emulsions were tested by varying the amount of surfactants. The effects of different surfactants used to produce emulsions with regular and modified soybean oil are discussed. The properties of these emulsions were tested by chemical and physical methods for stability and application as a metalworking fluid. Phase diagrams were created to determine the effect of oil, water, and surfactant ratios in the formation of emulsion. Cryo-SEM was used to probe the phase boundary and the bubble size.

2. Experimental

2.1. Materials

Crude soybean oil samples were supplied by Volga Oil Processing Company, Volga, South Dakota. Modified soybean oil was obtained from Urethane Soy Systems Inc., Princeton, IL. Ozone-modified and sulfur-modified oils were prepared in our laboratory. Several emulsifiers were tested in the formulations. Tween 40, a polyoxyethylene (20) sorbitan monopalmitate; Tween 60, a polyoxytheylene (20) sorbitan monostearate (non-ionic) surfactant; and Nikkol, a polyoxyethylene (40) sorbitan tetraoleate, were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Eccoterge 200, a nonionic ethoxylated fatty acid emulsifier, was obtained from Eastern Color and Chemical Company, Providence, Rhode Island.

2.2. Modification of soybean oil

Soybean oil was modified using ozone treatment and sulfurization. The sulfur modification reaction was carried out in a three-necked flask. Oil was heated to 140 °C while stirring with the help of a magnetic stirrer. Sulfur powder was added to the heated oil, and the reaction was continued for three hours. The resulting oil was centrifuged and filtered. The sulfur modified oil had a dark appearance and was more viscous than the starting oil.

The ozone modification of soybean oil was achieved with the help of an ozone generator, a L21 bench top model obtained from Pacific Ozone Technology, Brentwood, CA. The reactor cell components are made from titanium and ceramic, which are impervious to ozone. These machines produce pure ozone since there is no deterioration of internal materials. The feed gas, which is oxygen, was kept at 10 standard cubic feet per hour (SCFH). The ozone concentration was controlled with the help of a control lid and monitored with an ozone analyzer. Model H1-S was obtained from IN USA Inc., Needham, MA. Experiments were conducted by varying the concentration of ozone to monitor the effect of ozone. All experiments were performed at room temperature and standard atmospheric conditions. The oil obtained herein was used to prepare the emulsion.

2.3. Gel permeation chromatography (GPC)

A Waters 150 LC/GPC was used with a refractive index detector to measure the molecular mass. A Phenogel (Phenomenex, Torrance, CA) column (300 mm × 7.8 mm) with 500 μm particles was used for separation. HPLC grade tetrahydrofuran (THF) was used as the mobile phase. The experiment was carried out at room temperature with a solvent flow rate of 1 ml/min with 35 bars pressure. The refractive index versus the elution volume was obtained for each sample and correlated to the elution volume versus molecular weight for the polystyrene standard.

2.4. FTIR measurements

The FTIR measurements of the oil samples were conducted using a Nicolet 7000 series spectrometer. The samples were dissolved in chloroform, cast on a sodium chloride crystal to obtain a thin film, and dried in a chamber of nitrogen. FTIR spectra of these films were taken.

2.5. NMR spectroscopy

The NMR spectra of the oil and ozone-treated samples were obtained at 300 MHz using a Varian VXR300 instrument with a 12.2 ms (90°) pulse and an acquisition time of 2.0 s. The samples were dissolved in deuterated chloroform, and ^{1}H NMR spectra were obtained at room temperature.

2.6. Viscosity measurements

The viscosity of the oil samples was obtained using a Rheometric Scientific dynamic stress rheometer (DSR) with a couette geometry of cup diameter 32 mm and bob diameter 29.5 cm in stress sweep mode at room temperature (25 °C).

2.7. Preparation of emulsions

The stability of the emulsion system depends on the size of the droplets produced during emulsion formation. In order to produce an emulsion with an average diameter of several micrometers, a powerful homogenizer was used at a rotational speed of 2500 rpm for 10 min. Because the volume of the sample was found to influence the emulsification effectiveness, a minimal volume was placed in a closed vial to prevent turbulence during stirring and loss of material during homogenization. After emulsification, the samples were kept at room temperature. Emulsion stability was judged by the appearance and by observing phase separation, if any, during storage.

2.8. Phase diagrams

Phase diagrams were constructed for the ternary systems by titrating one component with different weight ratios of the other two. After each addition of the titrant (water), the sample was stirred and allowed to equilibrate for at least three hours before the phase equilibrium was observed. The formation of emulsion was inspected visually for each sample and the process continued until a stable emulsion was obtained [14]. The relative amount of each component was then calculated in wt.%. The ternary plots were obtained using SigmaPlot, SPSS Science, Chicago, IL.

2.9. Test for rust formation

The test for rust formation was conducted as follows based on a method available from the literature [15]. Two grams of cast iron chips were immersed in the emulsion and kept there for 10 min in a watch glass. The container was covered. After 10 min, the solution was removed by tilting the watch glass. The rust-preventive effect was observed visually after 24 h. A rating of 10 points corresponded to no appearance of rust.

2.10. Cryogenic scanning electron microscopy

The scanning electron microscope used was a Hittachi S-900, which contains a Hexland DN302 cold stage that keeps samples frozen during observation and allows for controlled sublimation. The emulsion samples were freeze-dried before observation under the microscope. Rapid freezing of the sample maintains the morphology of the emulsion. Each sample was placed onto a copper sample stub and immersed in liquid nitrogen. The samples were fractured while frozen and coated with platinum in a cryogenic condition and transferred into the SEM chamber for observation.

3. Results and discussion

The emulsions were obtained as a result of the association behavior of the surfactant components with the oil and water phases. The ability of a surfactant to form an emulsion is usually expressed in terms of hydrophilic–lypophilic balance (HLB) value of the surfactant. In practice, ethoxylates of fatty acid esters are found to be better surface-active agents for oil in water emulsions. The surfactant systems used in this study were selected from trial experiments. From experimental findings it was clear that the amount of surfactant needed for obtaining an isotropic single-phase emulsion differed for the various emulsion systems studied. Table 1 shows the different surfactant systems tested for emulsification. The emulsions obtained using Nikkol and Eccoterge 200 were found to be stable for all oils (umodified, sulfur modified, ozonized, and oxidized). However, the emulsions obtained for unmodified oil, were found to be stable only with Tween 60. For Tween 40, the emulsions with unmodified oil were moderately stable and phase separated after 48 h. The average droplet size for all the emulsion studied ranged between 7 and 10 μm.

The amount of surfactant required to obtain a stable emulsion was determined also in trial experiments. The modified oils needed more surfactant than unmodified oils. Unmodifed soybean oil needed approximately 3% by weight of either Nikkol or Eccoterge 200 for a stable emulsion. For both modified oils, the amount of the emulsifier needed increased to approximately 12%. This suggests that the unstable or reactive double bonds in the modified oils are reacted to form more stable or less reactive molecules in the modified oils that require more surfactant for emulsification.

The modified oils were more viscous when compared to regular oil. The viscosities and the molecular weights of the oils are shown in Table 2. In simulated machining tests to measure mist formation, modified oils performed bet-

Table 1
Properties of emulsifiers used for preparing oil-in-water emulsions

Trade name and class	Emulsifier composition	HLB[a]	Emulsion stability
Tween 40 (non-ionic)	Polyoxyethylene (20) sorbitan monopalmitate	15.6	Moderately stable for unmodified oil
Tween 60 (non-ionic)	Polyoxyethylene (20) sorbitan monostearate	14.9	Stable for unmodified oil
Nikkol (non-ionic)	Polyoxyethylene (40) sorbitan tetraoleate	11.4	Stable for all oils
Eccoterge 200 (non-ionic)	Ethoxylated oleic acid ester	∼12.0	Stable for all oils

[a] HLB is the hydrophile–lipophile balance of an emulsifier.

Table 2
Molecular weight and viscosity data for oils

Sample/reaction conditions	Number average mol wt. (M_n)	Weight average mol wt. (M_w)	Viscosity, Pa s (25 °C)
Soy oil	1363	1402	0.0628
1 h, Ozone treated	1645	2100	0.1021
3 h, Ozone treated	2030	3401	0.1583
Modified (oxidized) soybean oil	3558	19738	5.9128
Sulfur modified	2068	2548	0.2028

ter than unmodified oils [16] in terms of stability and mist generated. High viscosity of the continuous phase (the oil phase) contributes to the stability of the emulsion formed by lowering the mobility of the droplets in the emulsion, thus preventing the tendency to coalescence. This explains the higher stability of modified oil emulsions and the improved properties of these emulsions. Increased viscosity for both ozone-modified and sulfur-modified oils indicated that the double bonds in the oil molecules reacted with ozone or sulfur to form a more bulky molecule. This change was also visible in molecular weight determinations as shown in Table 2. The increase in molecular weight reflects the addition or branching reactions occurring at the double bond.

3.1. FTIR and NMR analysis

The FTIR spectra of soybean oil and ozone-treated oil are given in Fig. 1a and b. As can be seen from these figures, the spectrum of the modified oil differed from the original oil spectrum. The FTIR of ozone-treated oil gave peaks that support the ozonolysis reaction. The peaks at 3466, 1745, and 1104 cm^{-1} indicate the chemical changes occurring to the fatty acid chain during the reaction. The peaks at 2925 and 2851 cm^{-1}, which arise from C–H asymmetric stretch in CH_3, C–H asymmetric stretch in $–CH_2–$, and C–H asymmetric stretch in both $–CH_2–$ and $–CH_3–$, respectively, reduced markedly in intensity after ozonolysis. These reductions in peak intensity are due to the expected chain scission at C=C bonds of the fatty acid chains.

The change visible in the FTIR spectra of the ozonated oil in the broad peak between 3300 and 3600 cm^{-1} indicates the presence of hydroxyl groups in the ozonised oil. Ozone concentration and time of reaction are important to the ozonolysis reaction. It was found that the viscosity of the oil dropped and the properties of the oil changed considerably when ozonolysis continued longer than three hours.

NMR spectra were also used to examine the structural changes to oil molecules during ozone treatment. Proton NMR spectra of oil samples and ozone-treated oil were examined carefully (Fig. 2a and b) to study the spectral changes happening to the oil molecules. Spectra of the oil showed peaks due to methyl protons from fatty acids. The peaks, at ~5.4 ppm, were from protons attached to double-bonded carbon atoms in the fatty acid chain. It was clear from NMR spectra that the double bond peak decreased in intensity after ozonolysis. Also, a new peak was visible at 2.5 ppm for the ozonized oil sample. This represented a hydroxyl proton originating from the reaction of ozone with the fatty acid chain. The exact structures of these products are not interpreted from the NMR spectra, while spectroscopic evidence proves the presence of hydroxylated fatty acids. The NMR of sulfur-treated oil did not reveal any new peaks.

3.2. Rust inhibition properties

The ability to provide corrosion protection is important for a metalworking fluid. The emulsions were evaluated for rust formation on iron. None of the emulsions studied showed any rust formation within 24 h. Watanabe et al. [17] studied cutting fluid additives derived from undecanoic acid and reported similar observations. They also observed that triethanolamine salts of the fatty acids containing an ether, nitrile, hydroxyl, acetyl, or mercapto group at the ω-position had excellent antirust and antiwear properties. In the present investigation, the emulsions studied showed excellent antirust properties. These ozone- and sulfur-modified oil emulsions contain hydroxyl and mercapto groups, which may be responsible for the rust inhibition.

3.3. Phase diagrams

The different surfactants used in this study are indicated in Table 1. The Tween surfactants failed to produce a stable emulsion when used with modified oils. The Eccoterge and Nikkol surfactants produced stable emulsions with sulfur modified and oxidized oil samples respectively during machining operation. These two surfactants, when used with unmodified oils, engulfed the entire area. Phase diagrams were constructed using three surfactant systems to determine the limits for the thermodynamically stable phases when oil–water emulsions were prepared. The solubility areas formed were identified for all three systems. These are represented in Fig. 3a–c. From Fig. 3a, which is obtained using soybean oil and Tween 60, a polyoxytheylene (20) sorbitan monostearate (non-ionic) surfactant, the emulsion area was relatively broad when compared to the other two systems. Tween 60 had a higher HLB number as opposed to Eccoterge and Nikkol. The broader emulsion area clearly indicates the hydrophilic nature of the surfactant is visible from the phase diagram. In the case of sulfur-modified oil and Eccoterge, the emulsion area was not as wide (Fig. 3b) as that for Tween 60 and did not show a uniform trend.

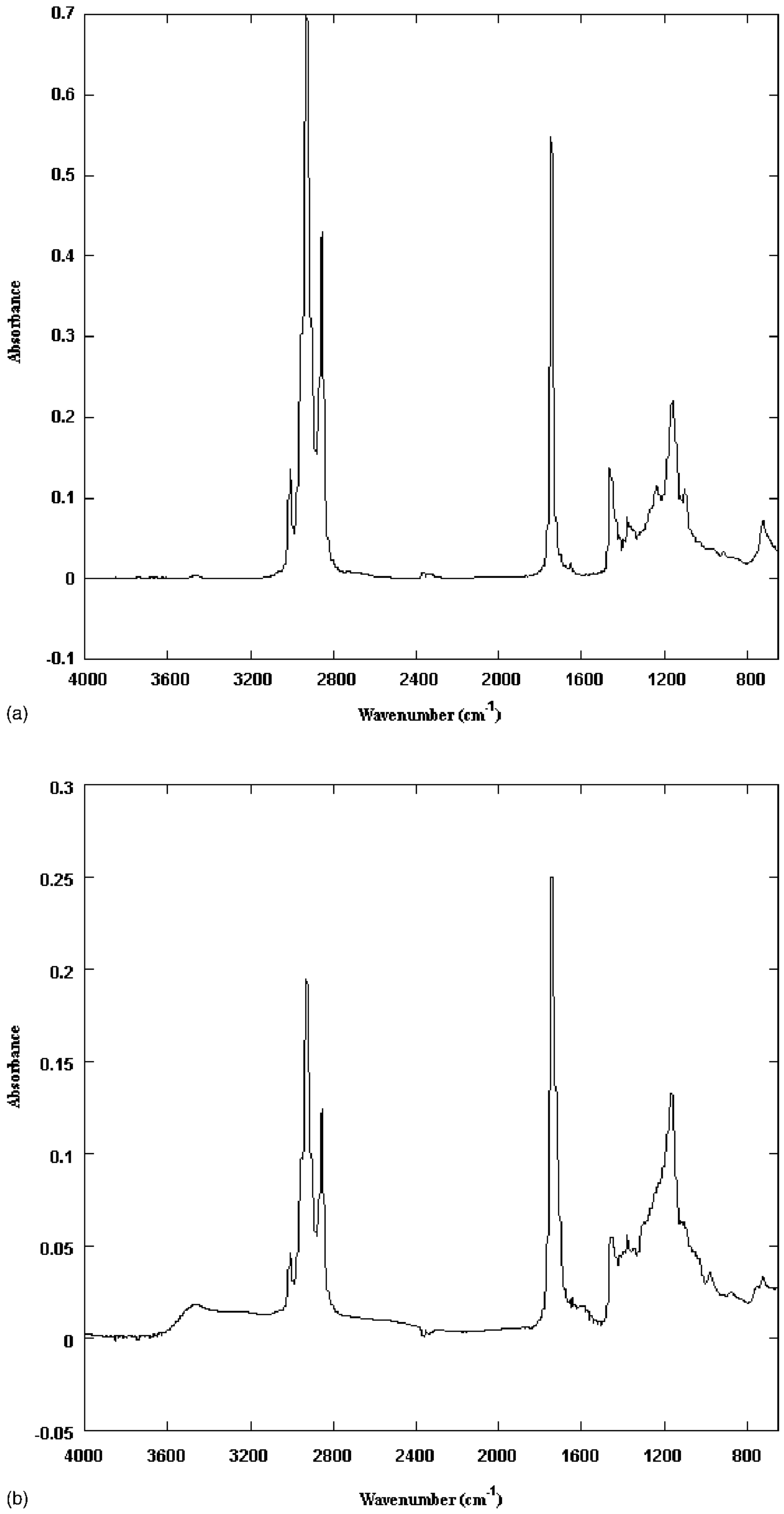


Fig. 1. FTIR spectra of: (a) soybean oil; (b) 3 h ozone treated soybean oil.

The diagram shows some cut-off regions that are sharp. The reason for this behavior is unclear. When Nikkol was used with oxidized oil, the phase diagram (Fig. 3c) was relatively smooth, showing clear regions of emulsion stability. In general, the phase diagrams indicate that the nature of emulsion obtained depended on the nature of the surfactant system employed. It also emphasizes the influence of modified oil on the area of solubility between the oil and water. This

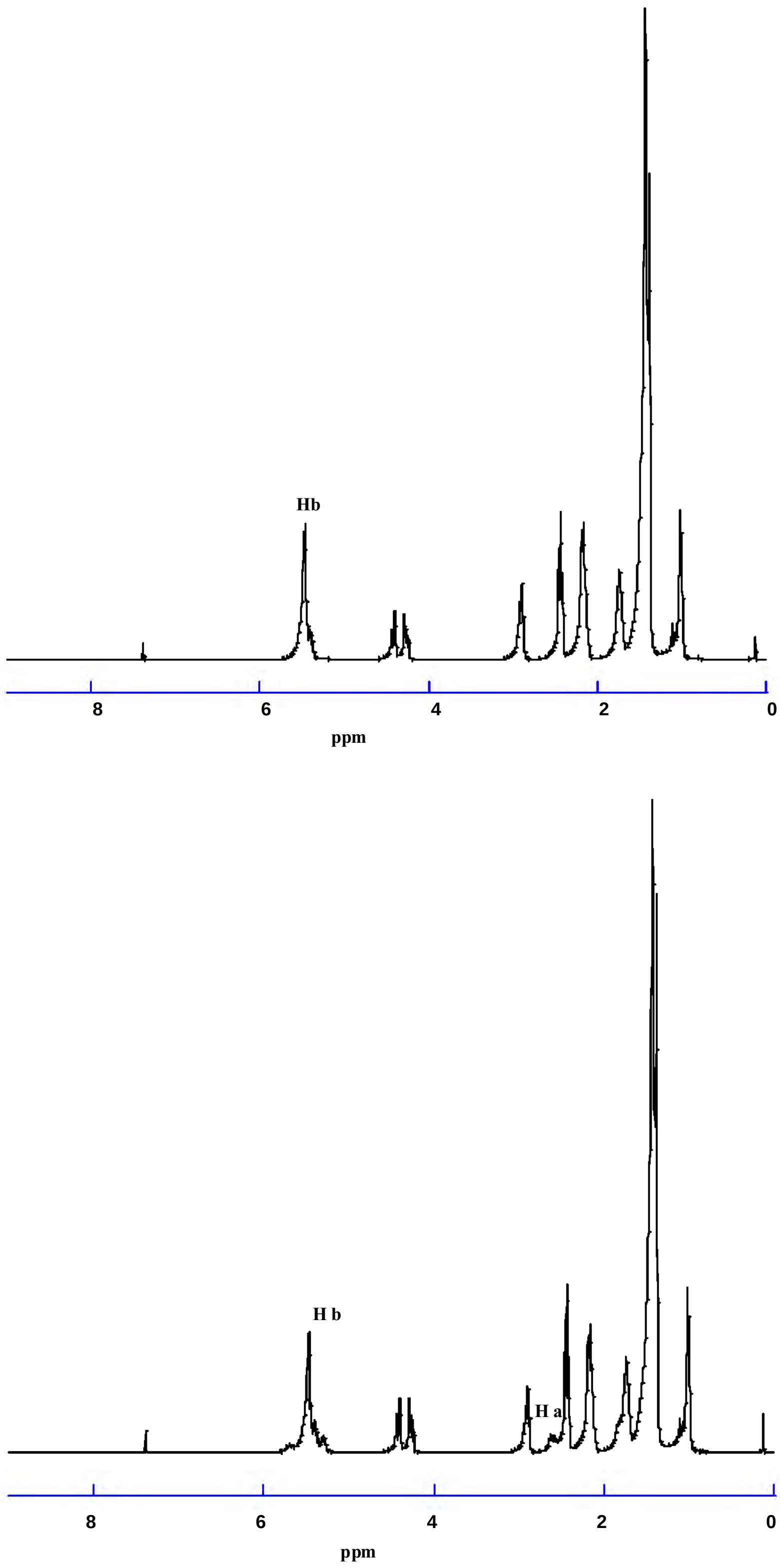
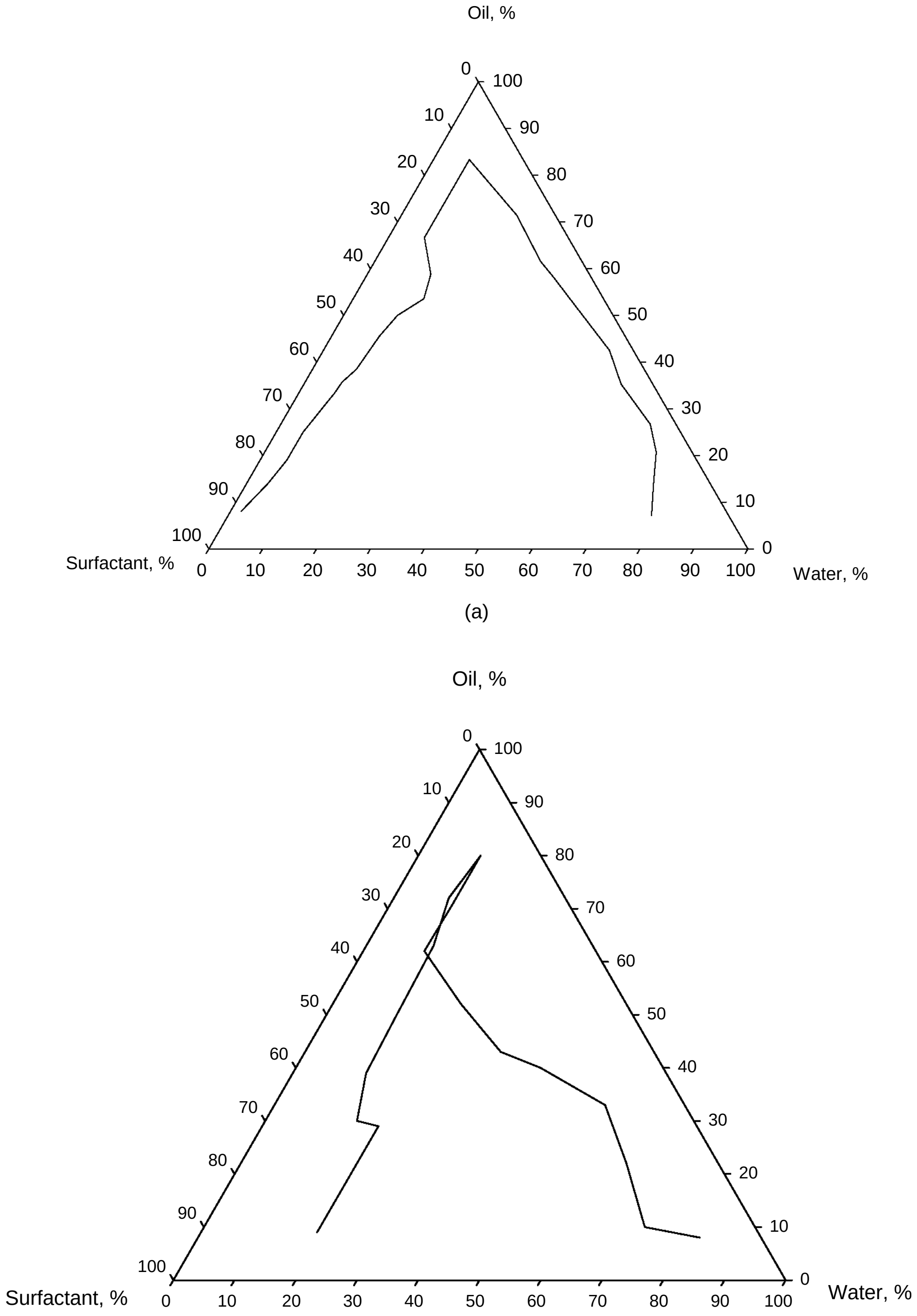


Fig. 2. (a) Proton NMR spectra of: (a) soybean oil; (b) ozone treated oil.

is particularly visible in Fig. 3b, where the sulfur-modified oil was used. The phase diagrams also indicate that the nature of the oil (modified versus unmodified) also influences the water solubility in the emulsion system.

A close examination of the surfactants employed reveals how these materials affect emulsion formation. The emulsion formation process involves a complex mechanism, where interfacial tension, adsorption phenomena, and the composition of surfactants play vital roles. Another important factor to be considered is that, at the oil–water interface, the components of the nonionic surfactant get fractionated between the oil and aqueous phases, i.e. these surfactants divide between oil and water. This phenomenon is well established by Crook et al. [18,19], who showed that when ethoxylates are dissolved in water, they get fractionated with the short-chain adducts being concentrated in the oil and the long-chain ethoxylates being concentrated in the water. Accordingly, immediately following the phase contact, various ethoxylate



(a)

(b)

Fig. 3. The isotropic emulsion areas of soybean oil–water-surfactant (a) (Tween 60) system at 25 °C. The relative amount of each component is given in wt.% along each axis. Each corner represents the pure (100%) component; (b) (Eccoterge) system at 25 °C. The relative amount of each component is given in wt.% along each axis. Each corner represents the pure (100%) component; (c) (Nikkol) system at 25 °C. The relative amount of each component is given in wt.% along each axis. Each corner represents the pure (100%) component.

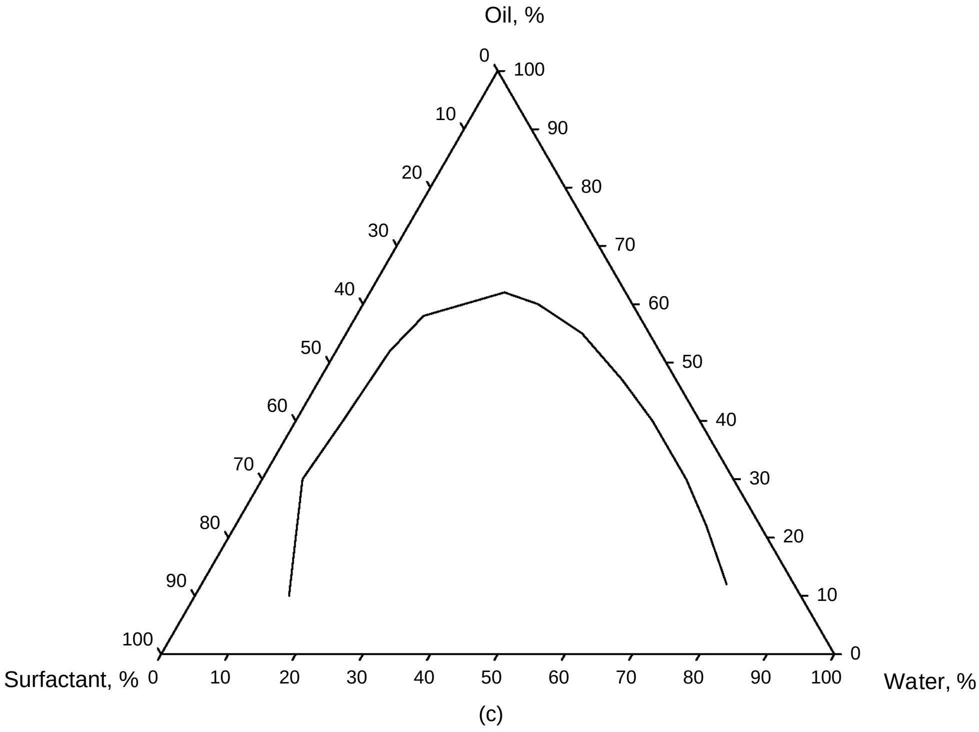


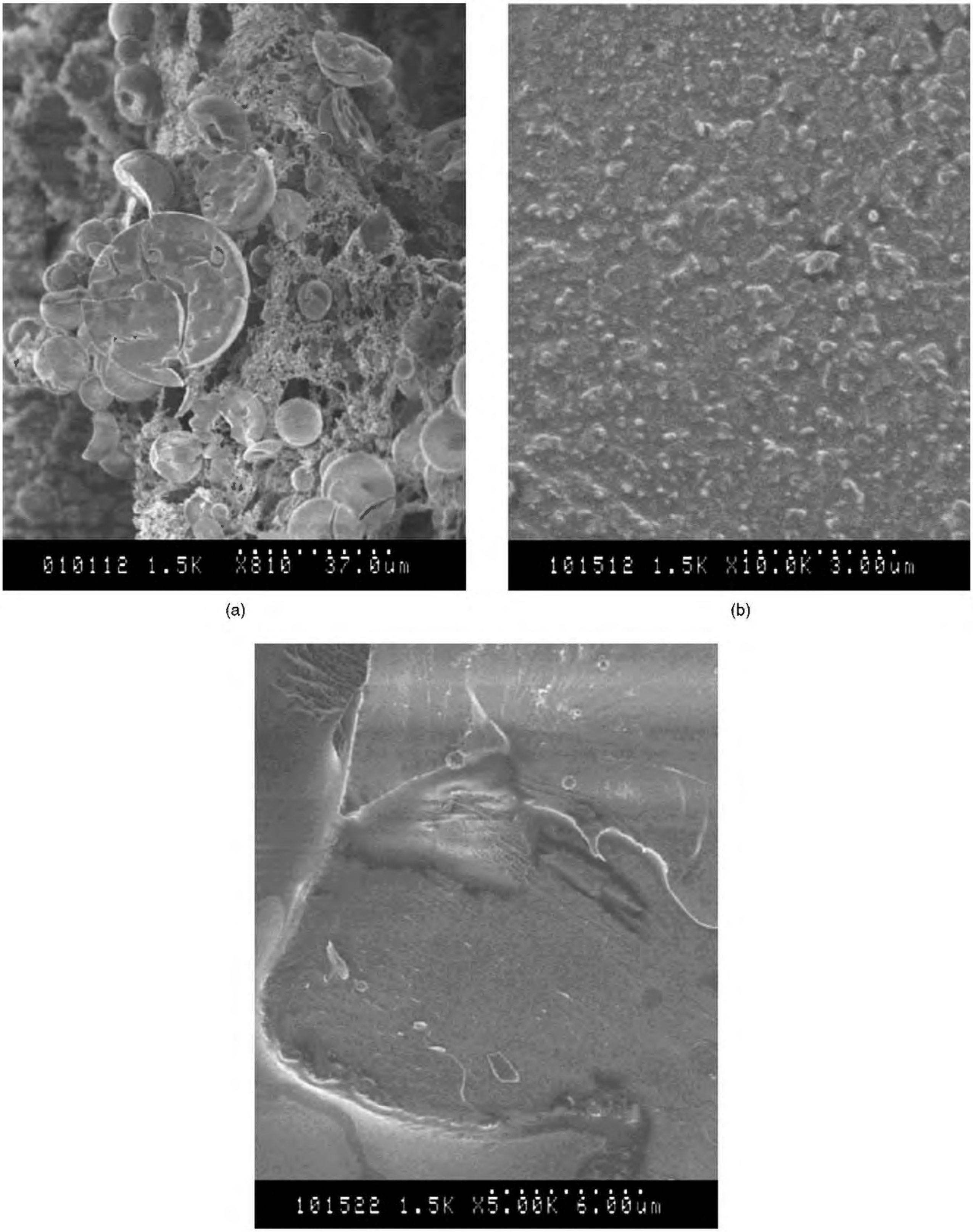
Fig. 3. (*Continued*).

adducts diffuse to the oil–water interface and compete for adsorption sites. The highly surface-active short-chain ethoxylates have a higher affinity for oil than for water [19] and will tend to migrate to the oil phase. Thus, during the first few minutes of emulsion formation, these diffusion and transfer processes occur until an equilibrium is reached. These processes reduce the interfacial tension, and a final equilibrium with emulsion formation is established. From this explanation, it is clear that the surfactant, which contains the largest weight fraction of oil-soluble species, may therefore be expected to partition more into the oil phase. This suggests that the emulsion stability and the process of emulsion formation depend mainly on the ethoxyl content of the surfactant and its distribution in the molecule. A difference in hydrophobe structure also affects surfactant performance. However, depending upon the ethoxyl content, the commercial families of surfactant behave different than normally expected. This could be due to the difference in the surface-active nature of the ethoxylates [20] and clearly explains the difference in nature of the three different surfactants used in this study. It also suggests that it is not only the number of ethoxylate groups, but also the nature of the groups that affects the emulsion formation. This explains the poor performance of the Tween system as opposed to the other two surfactants in this investigation.

As the surfactant concentration gradually increased, the rate of emulsion formation and the stability of the emulsion formed increased significantly. However, after reaching a sufficiently high concentration, the foaming of the emulsion became a hurdle. Foaming will adversely affect the performance of an emulsion used as a cutting fluid. Thus, it was necessary to determine the surfactant concentration that produced a stable emulsion without generating excess foam. As the concentration of the surfactant increased in the system, it was observed that interfacial tension was reduced at a faster rate. This indicates that the total number of surface-active adducts increases as the concentration of surfactant increases, bringing the interfacial tension to a minimum, which helps to obtain the emulsion at a faster rate. It should also be recognized that temperature also plays an important role with the concentration of the surfactant. As a general rule, the rate of emulsion formation will increase with increase in temperature. However, the effect of temperature was not investigated in this study.

3.4. Cryogenic SEM

Cryogenic SEM helps to elucidate the interaction between oil and water in the emulsion. The emulsion stability depends on the nature of the particle surface, the size distribution of the dispersed phase, and the stability of the dispersed phase. Direct observation, like cryo-SEM, helps to assess all these factors efficiently. The method used to prepare the sample was freeze fracture, which maintained the morphology or the relationship between the emulsion components. Selected samples are shown in Fig. 4a–c. Fig. 4a shows the morphology of the emulsion prepared with regular soybean oil with Tween 60. The two phases can be clearly identified from this figure. The water phase shows up as bright spheres in dark oil background [21]. The figure also helps to ex-



(a)

(b)

(c)

Fig. 4. Cryo-SEM of emulsion prepared with (a) soybean oil and Tween 60; (b) surfactant Eccoterge; (c) cryo-SEM of emulsion prepared with sulfur modified soybean oil and Eccoterge.

plain the droplet size, and the dispersed phase can be easily identified.

Fig. 4b represents the emulsion prepared using regular soybean oil and Eccoterge. The droplet size appears to be much smaller and uniform than the emulsions obtained using Tween 60, indicating a higher emulsion stability. This was true when the emulsion was examined visually, as these emulsions were more stable than the emulsions prepared using Tween 60.

Fig. 4c shows the morphology of sulfur-modified oil with Eccoterge as surfactant. The emulsion appears to be very uniform and stable and the different phases not easily identified. The thin film-like structure shows the stable emulsion phase rather than the oil and water phase. This clearly indicates that the interface is different for the emulsions prepared using modified soybean oil. Normally with such small oil content with respect to water, one would expect the water to be the continuous phase. However, with a large amount of surfactant and shear, it is possible to force this to be an oil continuous phase [22]. Fig. 4b shows a continuous phase of the oil (dark) with water (light) as the dispersed phase. The results indicate that modified oil emulsions are stable, which also supports the fact that the double bonds are broken during the oil modification process.

4. Conclusions

This study provides information useful for developing modified vegetable oil–water emulsion systems with different surface-active agents. Phase diagrams were constructed for these emulsions to determine the limits for the thermodynamically stable phases and indicate that the nature of emulsion obtained depends on the nature of the surfactant system employed. The phase diagrams presented in this study help to identify the isotropic emulsion regions. They also predict the region where an emulsion can be obtained by mixing the required components. Changes in FTIR and NMR spectra confirm chain scission at C=C bonds of the fatty acid chains. The viscosities and molecular weights of modified oils increased. Formation of hydroxyl groups during the ozonolysis reaction was observed. All the emulsions tested in this study showed good antirust properties. The cryo-SEM revealed the nature of phases in the emulsion and helped to examine the phase boundaries.

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References

[1] A.W. Schwab, L.E. Gast, Free radical addition of hydrogen sulfide to conjugated and nonconjugated methyl esters of vegetable oils, J. Am. Oil Chem. Soc. 47 (1970) 371–373.
[2] A.W. Schwab, L.E. Gast, W.K. Rohwedder, Nucleophilic addition of hydrogen sulfide to methyl oleate, methyl linoleate, and soybean oil, J. Am. Oil Chem. Soc. 52 (1975) 236–239.
[3] A.L. Bisio, M. Xanthos, How to Manage Plastics Wastes: Technology and Market Opportunities, Hanser Publishers, NY, 1995.
[4] F. Li, M.V. Hanson, R.C. Larrock, Soybean oil–divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships, Polymer 42 (2001) 1567–1579.
[5] L.A. John, D.J. Myers, In: D.R. Erickson (Ed.), Practical Handbook of Soybean Processing and Utilization, AOCS, St. Louis, MO/Champaign, IL, 1995.
[6] S. Asadauskas, J.M. Perez, J.L. Duda, Oxidative stability and antiwear properties of high oleic vegetable oils, Lubr. Eng. 52 (1996) 877–882.
[7] S.Z. Erhan, S. Asadauskas, Lubricant basestocks from vegetable oils, Ind. Crops Prod. 11 (2000) 277–282.
[8] V. D'Sousa, L. deMan, J.M. deMan, Polymeric behaviour of high-melting glycerides from hydrogenated canola oil, J. Am. Oil Chem. Soc. 68 (1991) 907–911.
[9] J. John, M. Bhattacharya, Properties of reactively blended soy protein and modified polyesters, Polym. Int. 48 (1999) 1165–1172.
[10] J. John, M. Bhattacharya, R.B. Turner, Characterization of polyurethane foams from Soybean Oil, J. Appl. Polym. Sci. 86 (2002) 3097–3107.
[11] J.M. Herdan, Rolling fluids based on vegetable oils, J. Synth. Lubr. 16 (1999) 201–210.
[12] J. Alander, T. Warnheim, Model microemulsions containing vegetable oils, J. Am. Oil Chem. Soc. 66 (1989) 1661–1665.
[13] Q. Xu, M. Nakajima, H. Nabetani, S. Iwamoto, X. Liu, The effects of ethanol content and emulsifying agent concentration on the stability of vegetable oil–ethanol emulsions, J. Am. Oil Chem. Soc. 78 (2001) 1185–1190.
[14] S. Friberg, J.H. Fang, Temperature dependence of the solubility areas for w/o microemulsions with nonionic/anionic surfactants, J. Am. Oil Chem. Soc. 61 (1984) 801–804.
[15] S. Watanabe, H. Nakagawa, Y. Ohmori, T. Fujita, M. Sakamoto, T. Haga, Characteristic properties of cutting fluid additives derived from half esters of dimer acids, J. Am. Oil Chem. Soc. 73 (1996) 807–809.
[16] S.W. Kim, P.C. Raynor, M. Bhattacharya, submitted for publication.
[17] S. Watanabe, T. Fujita, M. Sakamoto, I. Shirakawa, H. Kawahara, Characteristic properties of cutting fluid additives derived from undecanoic acid, Ind. Eng. Chem. Res. 28 (1989) 1264–1266.
[18] E.H. Crook, D.B. Fordyce, G.F. Trebbi, Molecular weight distribution of nonionic surfactants, J. Phys. Chem. 67 (1963) 1987–1994.
[19] E.H. Crook, D.B. Fordyce, G.F. Trebbi, Moleular weight distribution of nonionic surfactants, J. Colloid Sci. 2 (1965) 191–204.
[20] K.W. Dillan, E.D. Goddard, D.A. McKenzie, Examination of the parameters governing oily soil removal from synthetic substrates, J. Am. Oil Chem. Soc. 57 (1980) 230–237.
[21] R.J. Mikula, V.A. Munoz, Characterization of emulsions and suspensions in the petroleum industry using Cryo-SEM and CLSM, Colloids Surf. 174 (2000) 23–36.
[22] R.J. Mikula, Personal Communication, 2003.