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Function and performance of silicone copolymers: 1. Syntheses of polysiloxane-containing copolymers and their absorption phenomena under extreme pressure

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Two types of multifunctional copolymers containing siliconized-acrylate monomer (SAM) were synthesized: copolymer SNS (containing SAM, stearyl acrylate and N,N-dimethylaminoethyl acrylate monomers) and copolymer SAS (containing SAM, stearyl acrylate and an amine salt of acrylic acid). Their structures were confirmed by ^1H nuclear magnetic resonance, and their adsorption behaviours on metal surface were characterized by electron spectroscopy for chemical analysis. It was found that both synthesized copolymers were good viscosity index improvers and have superior anti-wear properties when used in boundary lubrication conditions. Scanning electron microscopy results indicated that these two copolymers formed significantly thick adsorption layers compared with conventional anti-wearing agents, and the chemisorption occurred more in the case of the SAS additive in the case of the SNS. © 1997 Elsevier Science Ltd.

(Keywords: polymeric additives; antiwear properties; boundary lubrication conditions)

INTRODUCTION

Lubricants have been widely used in cars and machines for hundreds of years. There is a great deal of interest both in fundamental lubricant research and investigation into addition applications for lubricants due to their economic importance[1,2]. Lubricants act primarily to decrease the friction coefficient. Lubricants also have to exhibit many additional properties such as detergency[3], dispersibility[4], anti-foaming action, and thermal and oxidative stability[5]. Thus, many types of additives are compounded to prepare a commercial lubricant to satisfy these rigorous requirements.

Extreme-pressure additives act to form a lubricating film to prevent direct contact between metal surfaces under a sudden increased loading pressure[6]. These additives have to adsorb physically on to the metal surface and then chemically react; thus, functional groups such as sulfide, amine or carboxylic groups are usually contained in these additives to achieve these purposes[7]. The usual extreme-pressure additives are sulfur- or phosphorus-containing organic compounds; thus, the lubricating film on the metal surface is a thin molecular monolayer[8,9]. If the extreme-pressure additive is a polymer, the film on the metal surface would be constituted by random coils of the polymer chains, and the film would be much thicker and more effective in preventing contact with the metal surfaces.

Also, additives are compounded in the lubricant to absorb physically and chemically on to the metal surfaces to lower the friction coefficients[10]. It is known that silicone compounds can lower surface tension and reduce the friction coefficient. It would be interesting to synthesize a copolymer as a multifunctional, anti-wear additive which contains both silicone segments and functional groups which can physically adsorb on, or chemically react with, the metal surfaces.

In this study, polysiloxane-containing acrylic monomer and acrylic monomer with functional groups (either amine or carboxylic acid) incorporated were copolymerized with the acrylate of a long chain alcohol. These copolymers were characterized, and their solution in mineral oil was used as a lubricant for studying their lubricating ability. The adsorption layer of these copolymers on a metal surface was characterized by scanning electron microscopy (SEM) and electron spectroscopy for chemical analysis (ESCA); the results were then interpreted and correlated with the copolymer structure and their lubricating ability. In addition, the viscosity-improving properties of these copolymers were investigated.

EXPERIMENTAL

Materials

N,N-Dimethyl aminoethyl acrylate (DAA; TCI, EP grade), acrylic acid (AA; Ishizu, EP grade), steryl

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acrylate (SA; Aldrich), 2-hydroxyethyl methacrylate (2-HEMA; Aldrich), 2,2'-azobis(isobutyro)nitrile (AIBN; TCI, EP grade), siloxane oligomer SY-231 (Wacker), tributylamine (Merck, EP grade) and tripropyl titanate (TPT; ICI) were used without further purification. Base oil and commercialized lubricating oil 15W-40 were obtained from Chinese Petroleum Corp.

Synthesis of siliconized acrylic monomer (SAM)
(Scheme 1)

In a 250 ml four-necked reactor were placed quinone, 24 g of 2-HEMA, 90 g of SY-231 and 0.5 g of TPT. The reaction was stirred at *ca* 140°C until a calculated amount
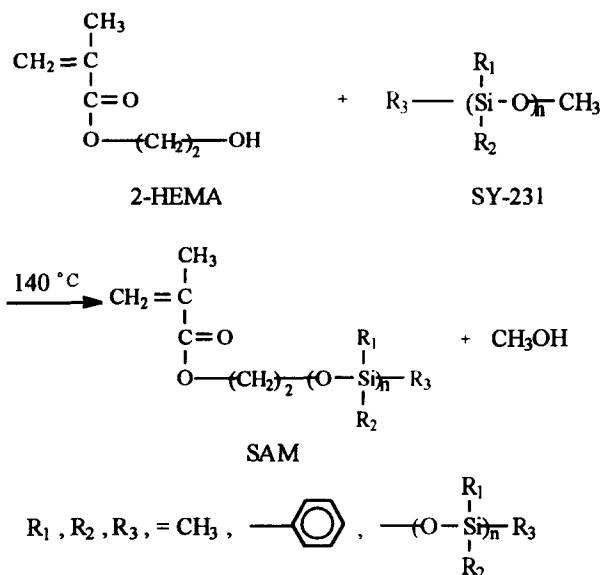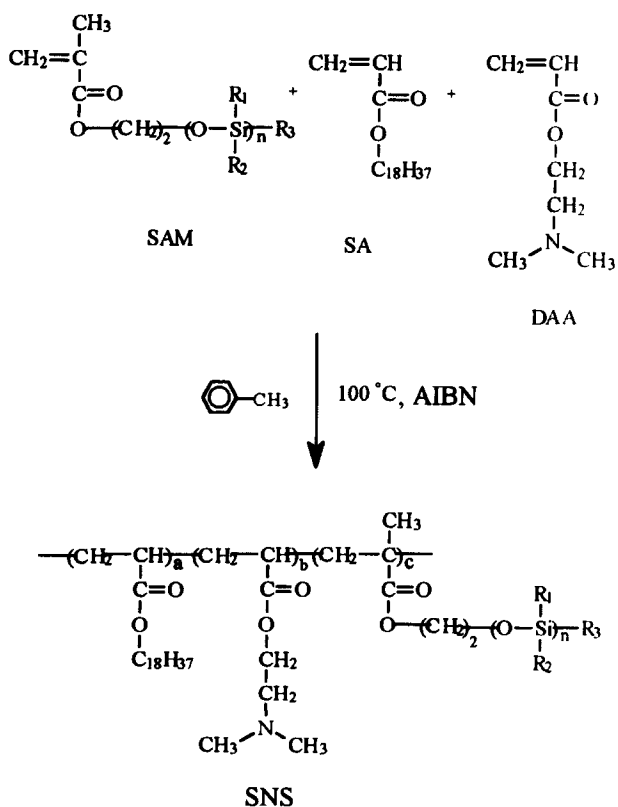
of methanol was collected. The yield based on 2-HEMA was about 90%.

Synthesis of poly(siliconized acrylate–N,N-dimethyl-aminoethyl acrylate–steryl acrylate) (Scheme 2)

In a 250 ml four-necked reactor, was dissolved 5 g of SAM and 10 g of SA in 68 g of toluene. After raising the temperature to 100°C, 2 g of DAA and 0.0051 g of AIBN were added to the reactor along with a low stream of nitrogen. The reaction was run for 3 h and poured into 500 ml of acetone to precipitate the polymer. For convenience, this copolymer is labelled SNS.

Synthesis of poly(siliconized acrylate–acrylic acid–steryl acrylate) (Scheme 3)

This reaction was run in a similar manner to that described above except that AA was added instead of DAA. After 3 h, the solution was neutralized by tributyl-amine and stirred for 6 h. The reaction mixture was then poured into 500 ml of acetone to precipitate the polymer. This copolymer was designated as SAS.

Polymer characterization: anti-wear tests on the polymeric additives in an oil system

A measured amount of polymeric additive was
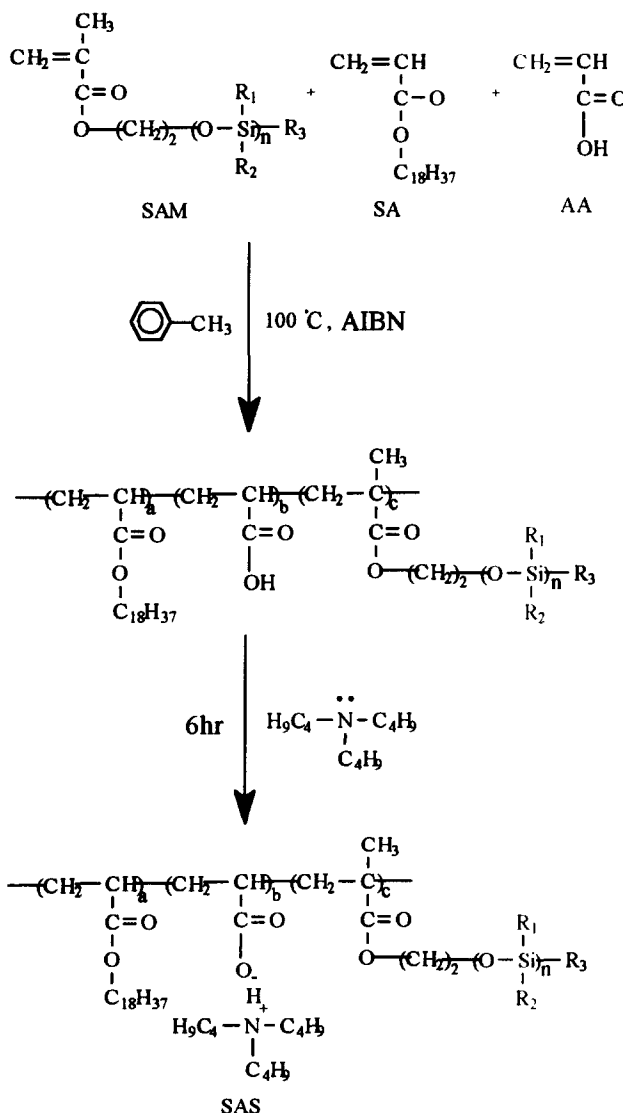
Scheme 1

Scheme 2

Scheme 3

dissolved in 100 g of base oil. A roller with its metal plate was immersed in the oil solution to test its anti-wear ability. The voltage of electrical contact resistance, the temperature of the oil, and the friction coefficient were recorded by a computer. The weight loss of the roller was measured. The surface of the worn roller was then examined by SEM and ESCA. The surfaces of the worn rollers were sputter-coated with gold and investigated using a Jeol J × A-840 scanning electron microscope.

ESCA surface analysis was carried out using a VG Instrument X-ray photoelectron spectrometer. Mg K_α radiation was used as the X-ray source, and the photoelectron peaks from the samples were numerically fitted using Lorentzian curves with an integral background subtraction and analysed at an angle of 45° to the surface. The adventitious C 1s signal at 284.6 eV was used to calibrate the charge-shifted energy scale. The X-ray spot size was 600 mm and the resolution was always about 0.8 eV; the spectra represent original experimental data

recorded to an accuracy of 0.2 eV. In addition, the spectra have been deconvoluted for chemical identification using 100% Gaussian peaks.

RESULTS AND DISCUSSION

Polymer synthesis

The main objective of this research was to develop multifunctional polymeric additives for lubricating oils. These additives are mainly used as, for instance, viscosity index (VI) improvers, anti-wear additives, antifoaming agents and detergents and dispersants. To impart these specific properties to the lubricant, copolymers containing siliconized acrylate monomer and some monomers such as AA, an ester of AA, an amino ester of AA or an amine salt of A were synthesized. The siliconized acrylate monomer was first prepared as the basic part of these copolymers due to its superior properties in terms of thermal stability, VI and defoaming ability. Next, two
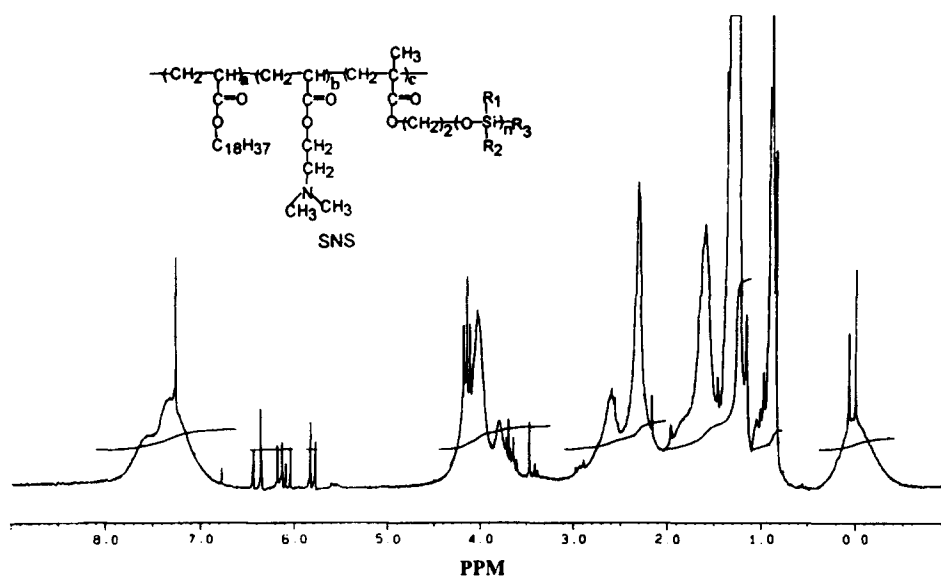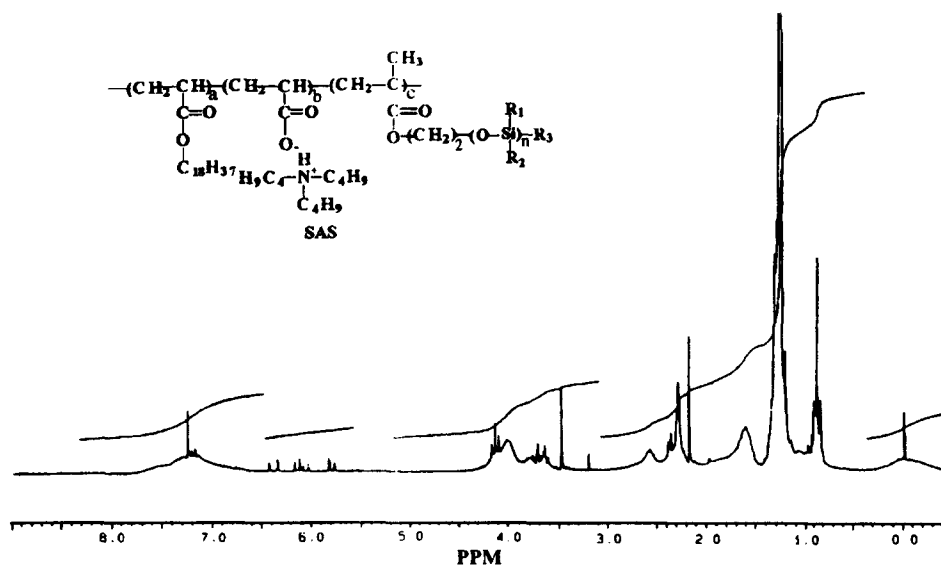

Figure 1 ¹H n.m.r. spectrum of SNS copolymer

Figure 2 ¹H n.m.r. spectrum of SAS copolymer

types of copolymers were synthesized. They were designated as SNS and SAS as described previously.

Both SA and DAA monomers incorporated into the SNS copolymer enabled this copolymer to function not only as a VI improver, but also as an anti-wear additive and detergent and dispersant[11,12]. The transformation into an amine salt for the SAS copolymer was based on the same objective. Both types of polymeric additives were then characterized with ^1H nuclear magnetic resonance (n.m.r.) spectroscopy. Typical spectra for both types of copolymers are shown in *Figures 1* and *2*, respectively. As seen in both spectra, it is evident that siliconized acrylate monomer was successfully synthesized and incorporated into both copolymers. For both copolymers, the resonance peak at approximately 0 and 7.0–7.5 ppm is associated with the protons of the methyl groups and the phenyl rings on the silicon atom of SY-231 while the peak at 0.9–1.0 ppm represents the protons of the methyl group on SA. Furthermore, the peak at *ca* 2.5 ppm (*Figure 1*) arising from the protons of two methyl groups on the nitrogen atom indicates the presence of DAA in the SNS copolymer. On the other hand, the resonance peak at 3.5 ppm presented in *Figure 2* is ascribed to the protons of the methylene groups on the nitrogen atom of the acrylic amine salt. It is apparent that both copolymers were successfully synthesized. The intrinsic viscosities (η) of both copolymers are given in *Table 1*.

Polymer characterization

The VI of the lubricant is most probably the most important factor when selecting a lubricant for any application[13]. A high VI value indicates a relatively low rate of change of viscosity with temperature; a low VI indicates a relatively high rate of viscosity with temperature[14]. Most multigrade engine oils and certain synthetic oils have VI values much higher than 100. In the present studies, the viscosity index of the base oil is *ca* 95. After addition of various concentrations of these

additives, VI values increased up to 100–120. The VI values for various concentration of both types of synthesized polymeric additives are summarized in *Table 2*. It can be seen that the VI values for the SNS system are generally higher than those for the SAS system. Since the SNS copolymer has higher inherent viscosities (η), it was felt that higher molecular weights of additives have more striking effects on the improvement of VI of the lubricating oil.

In the evaluation of the anti-wear properties of both types of copolymeric additives in the lubricating oil, some performance tests under similar service conditions were carried out by means of a multifunctional wear-testing machine[15,16]. Typical results from the testing are shown in *Figures 3* and *4*, respectively. As seen in both figures, decreasing friction coefficients are accompanied by increasing voltages, indicating the formation of organic films on metal surfaces and increases in film thicknesses with the testing time. The commercialized lubricating oil (I5W-40) chosen shows a similar trend (*Figure 5*). Nevertheless, the amount of wear produced during testing for the commercial product is much higher, as compared to both polymeric additives in terms of lubricating ability, as illustrated in *Table 2*. Hence, it is evident that the additives added to the commercial product result in inferior anti-wear properties. However, additives used to improve the performance of lubricants may be classified into two groups: (a) mild wear- and friction-reducing additives, and (b) extreme-pressure additives. Thus, further experiments were carried out to differentiate between the mechanisms for these types of additives under the same lubrication test conditions.

Among the various characterization techniques which are suitable for surface analysis of these worn surfaces, ESCA has emerged as the most powerful tool[17,18]. For the commercial oil product, the ESCA results, as given in

Table 1 Basic properties of SNS and SAS copolymers

Polymer	Monomer ratio SAM/DAA/SA	SAM/AA/SA	Silicone ratios (wt%)[a]	(η)[b]
SNS	5/2/10	–	12.26	0.243
SAS	–	5/2/10	8.68	0.203

[a] Wt% based on polymer weight and measured by elemental analysis
[b] Inherent viscosity measured by Ubblehode viscosimeter

Table 2 Viscosity index values and wear amounts after anti-wear tests for SNS and SAS at various concentrations

Polymer	Concentration[a] (%)	Viscosity index[b]	Wear amount ($\times 10^{-5}$)[c]
SNS	1	132.1	71
	3	130.9	77
	5	137.5	81
SAS	1	125.9	79
	3	116.1	84
	5	92.0	82
15W/40		100.0	373

[a] Commercial product 15W/40 (Chinese Petroleum Corp.) Wt% based on base oil
[b] Calculated by ASTM-2270 method
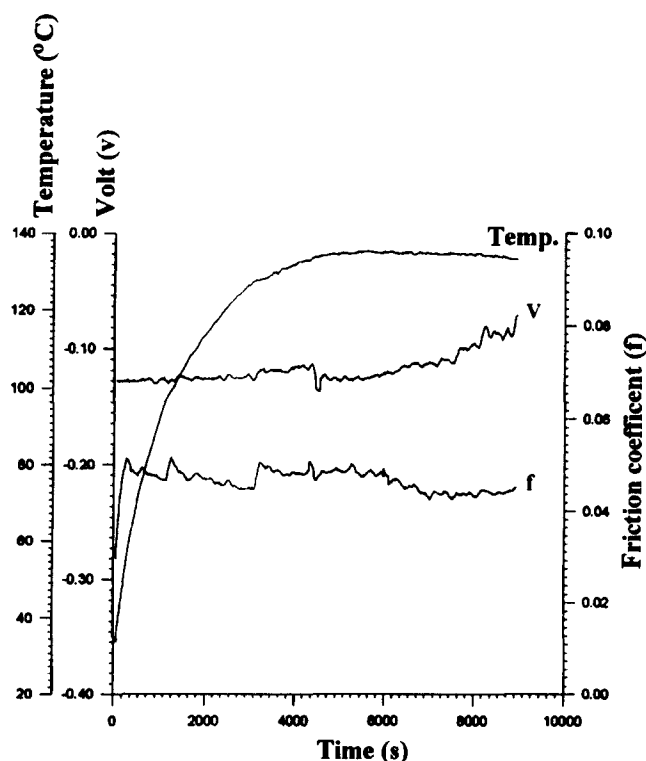[c] Weight difference before and after anti-wear tests

Figure 3 Anti-wear test results for SNS (3.0 wt%) additive under 400 kg load and 450 rev min^{-1}
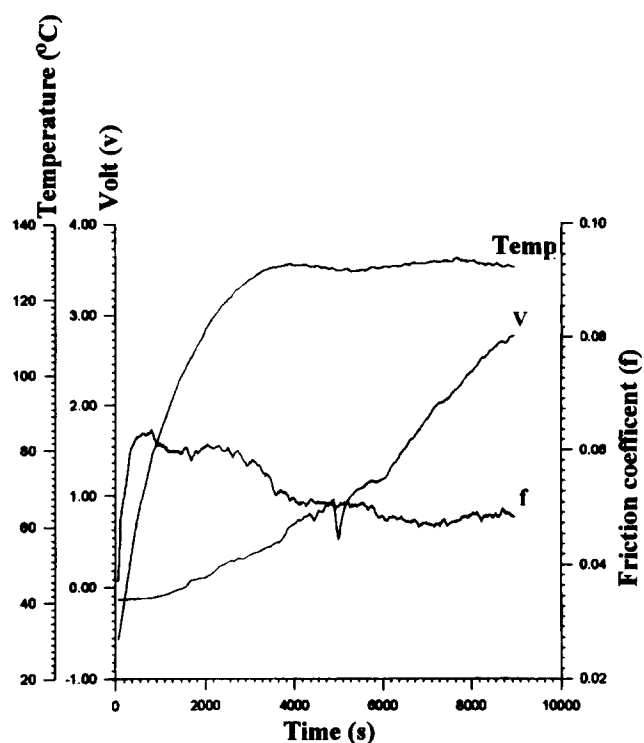
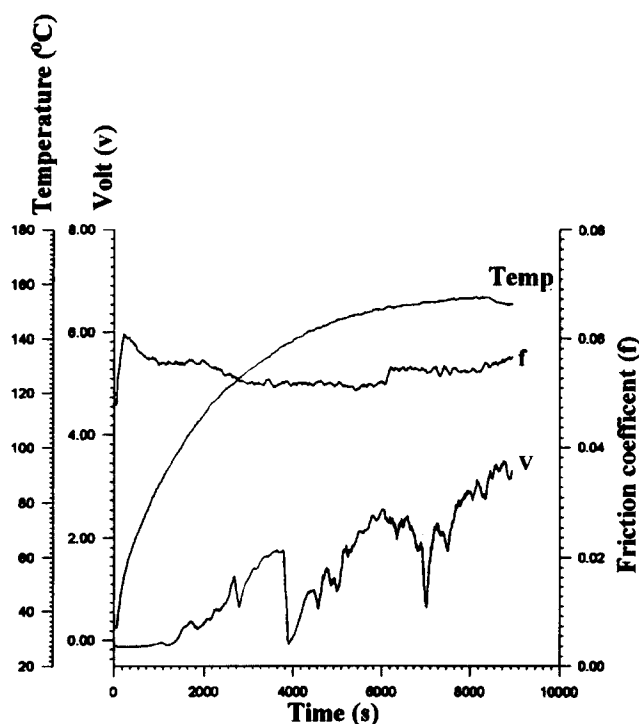**Figure 4** Anti-wear test results for SAS (3.0 wt%) additive under 400 kg load and 450 rev min^{-1}

Figure 5 Anti-wear test results for the commercial oil product 15W-40 under 400 kg load and 450 rev min^{-1}

Table 3 ESCA results for rollers' surfaces after anti-wear tests for SNS and SAS

Sample	Fe	O	C	Si	N	P	S
SNS (3%)	709.9	529.7	284.6	102.1	398.1	—	—
	714.2	530.8			399.3		
		531.8			400.7		
SAS (3%)	710.7	531.6	284.6	101.5	399.5	—	—
	715.5						
Commercial Product 15W/40	706.5	—	—	—	—	132.0	170.5
	709.1						169.5
	711.9						

^{a} Possible compounds are Fe_2O_3: 711; Fe_3O_4: 711.2; FeOOH: 711.5; FeO: 710.4; PMMA: 533.9; $(CH_2)_n$: 284.6; $(Me_2SiO)_n$: 101.5; $(MeSiO)_5$: 101.5; $Ph_3SiOSiPh_3$: 101.5; $BuNH_2$: 398.8; $PhNH_2$: 399.2; Ph_3PO: 132.2, K_2HPO_4: 132.2, Na_3PO_4: 132.2; Bu_4PCl: 131.9; PhPS: 131.9 (Me: methyl; Ph: phenyl; Bu: butyl), $Fe_2(SO_4)_3$: 168.9
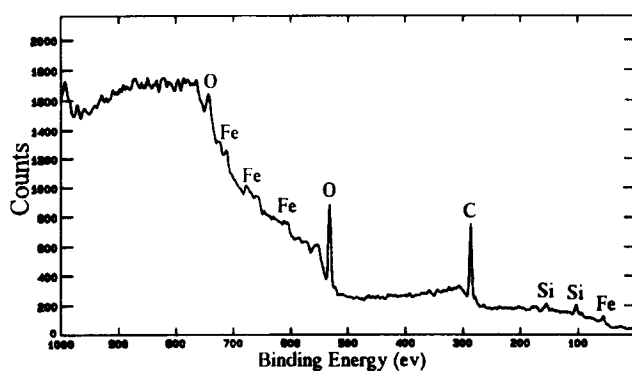

Figure 6 ESCA spectrum of the roller's surface after the anti-wear test was complete for the SNS (3.0 wt%) copolymer additive system
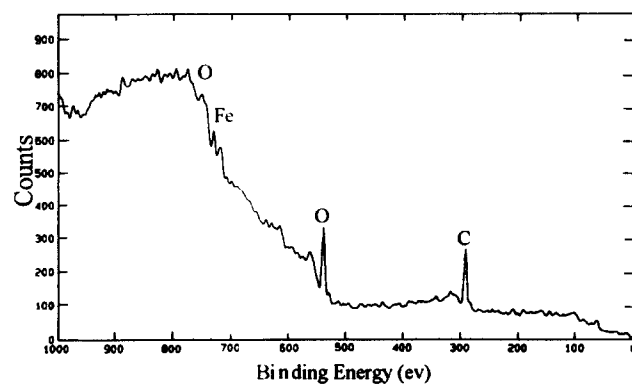

Figure 7 ESCA spectrum of the roller's surface after the anti-wear test was complete for the SAS (3.0 wt%) copolymer additive system

Table 3, show a peak at 132.0 eV, indicating the presence of a phosphorous compound. Moreover, the unresolved peaks at 169.5 and 170.5 eV are assigned to $Fe_2(SO_4)_3$ while peaks at 706.5, 709.1 and 711.9 eV are assigned to the formation of FeS_2, $Fe(SO_4)_2$ and Fe_2O_3 compounds. This implies that chemical reactions have occurred with the commercial product. Consequently, phosphorous- and sulfur-containing additives in this lubricating oil

have reacted with the metal surface during the lubrication test[19,20]. In contrast, no chemical reactions have been observed for either type of synthesized polymeric additive. Combining these results, we conclude that commercial and synthesized additives have different end uses in terms of lubrication. The primary function of the additives in the commercial lubricating oil is as an extreme-pressure additive, while the synthesized polymeric additives are more powerful as anti-wear additives under mild wear conditions.

In addition, the adsorption behaviours of both synthesized polymeric additives might also be illustrated

by ESCA studies. In the case of the SNS sample, as seen in *Table 3* and *Figure 6*, the peak at *ca* 284.6 eV represents the carbon of methylene groups $-(CH_2)_n-$. The peak around 101–104 eV may indicate the presence of silicon in $-(SiMe_2O)_n-$ (where Me represents the methylene group) or $-(Si\phi_2O)_n-$ (where ϕ represents the phenyl ring). At *ca* 531 eV, a much stronger peak is observed, which denotes the presence of oxygen from oxides and indicates that oxidation reactions have occurred on the metal surface; hence, Fe_2O_3 or Ni_2O_3 has been formed. Around 398–400 eV, small peaks confirm the presence of the nitrogen atom. Finally, small peaks at 710–714 eV can be assigned to the iron formed after oxidation reactions. Peaks observed in this region may be assigned to Fe_2O_3, Fe_3O_4 or FeOOH. The ESCA results for the case of SAS materials show similar trends (*Figure 7*).

Referring to our lubrication test results, we can derive some important conclusions. First, our results reveal that both synthesized polymeric additives exhibit superior anti-wear properties under boundary lubrication conditions. During the lubrication tests, the surface asperities of the rollers were initially coated with films of oxide, i.e. iron oxide on the steel surface, nickel oxide on the nickel surface, etc. When such asperities rubbed together, their tendency to adhere was relatively low. As a result, small amounts of wear were observed as compared to the case of the commercial product. Subsequently, as the load increased and the temperature rose, these oxide films were removed by rigorous rubbing, which resulted in high friction and severe wear for the exposed metal surfaces. As stated previously, this is regarded as the extreme-pressure case, whereas the small amount of wear obtained in both cases where polymeric additives were used might indicate that the loads under extreme-pressure lubrication conditions were not applied for long enough. Consequently, the oxide films were not fully removed and only small amounts of reacted phosphorous and sulfur compounds were observed for the case of the commercial product. Therefore, additives used in the commercial product mainly function as extreme-pressure additives, while the
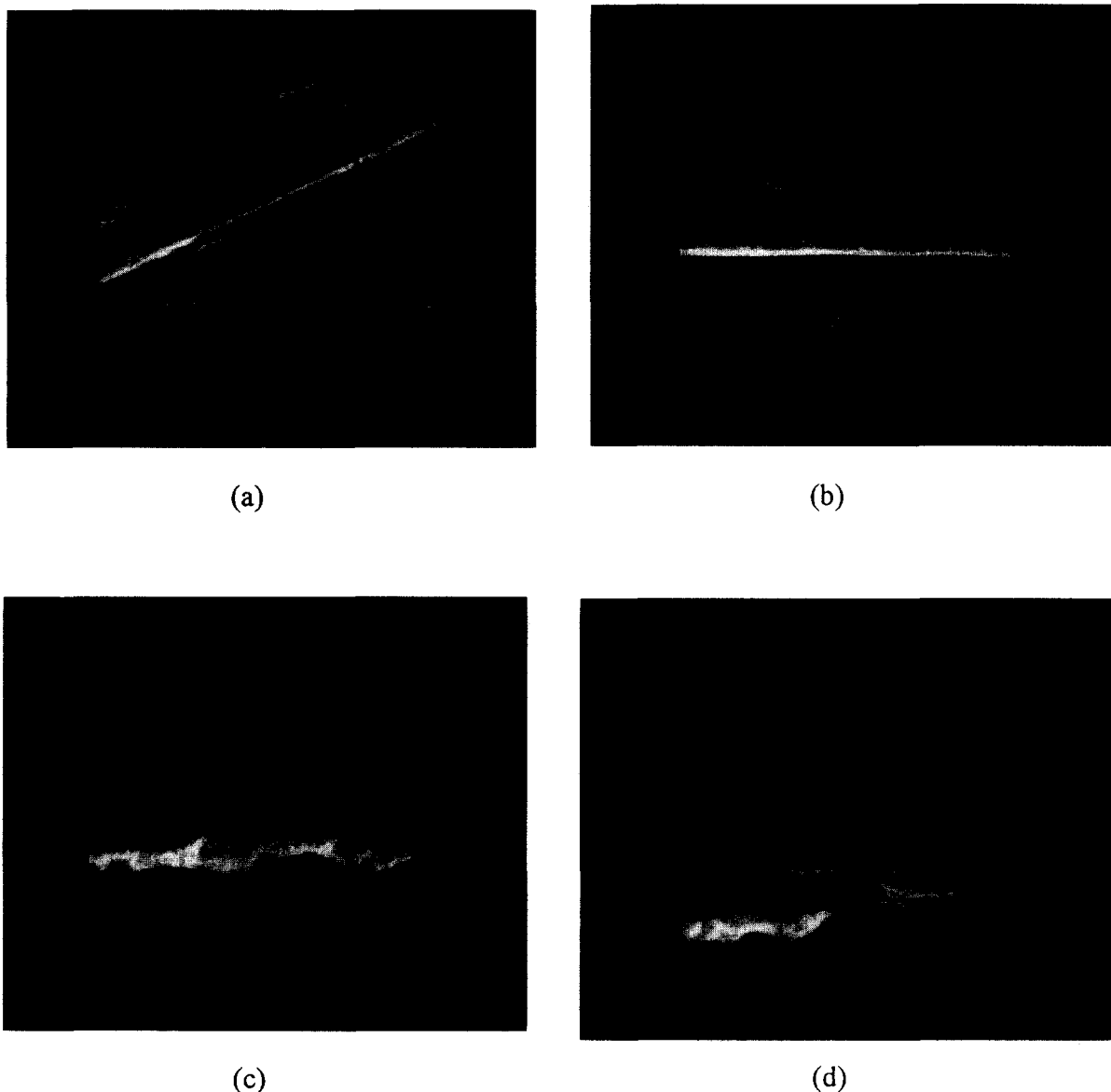

(a)

(b)

(c)

(d)

Figure 8 SEM micrographs of rollers' surfaces after anti-wear tests: (a) control; (b) the commercial product 15W-40; (c) SNS (3.0 wt%); (d) SAS (3.0 wt%)

synthesized polymeric additives are mainly used in boundary lubrication conditions.

Next, for the synthesized additives, the peak at 284.6 eV is strong evidence for the polymeric additives being adsorbed on the metal surface. It seems that films on the metal surfaces were composed of two parts: (1) the metal oxide film, and (2) the adsorbed film. It is well known that there are two adsorption mechanisms under boundary lubrication conditions. One is physical adsorption, and the other is chemisorption. Since the rollers tested have been cleaned with detergents, the films adsorbed on the metal surfaces may be fully adsorbed by chemisorption. Furthermore, it appears that chemisorption occurred to a greater extent with the SAS additive compared to the SNS additive because the SAS copolymer was negatively charged in the lubricant and more readily interacted with the metal surface by electrostatic attraction. Referring to our anti-wear tests results, as given in *Figures 3* and *4*, the same phenomena may be present. Our data indicated that physical adsorption occurred more rapidly than did chemisorption. Consequently, a film was formed instantly and the voltage rose up quickly, as seen in the case of the SNS copolymer, whereas the film formed by chemisorption was formed more slowly; hence, the voltage reached its limiting value over a longer time. In the case of the commercial product, the film formed on the roller's surface may be composed of three parts: (1) the metal oxide film, (2) the adsorbed additive films, and (3) the film formed by chemical reaction. The third part was confirmed by the formation of compounds containing iron and sulfur or phosphorous.

SEM examinations have also been carried out to examine the films formed on the metal surface. *Figure 8* shows the SEM micrographs after anti-wear tests were completed for the commercial lubricant, the SNS copolymer, the SAS copolymer and a control (no additives present). It was seen that no film was formed on the roller's surface for the control. In the case of the commercial lubricant, a homogeneous, very thin film was observed. Since it has been shown in the literature that extreme-pressure additives often lead to polishing of a metal surface, this result is not surprising. In contrast, both synthesized copolymeric additives produced thicker films on the metal surfaces, with the SAS sample forming a thicker film compared to the SNS sample. This testifies to the fact that more chemisorption occurred with the SAS additive.

CONCLUSIONS

Two types of polymeric additives were prepared and characterized with regard to their lubricating ability. The

^{1}H n.m.r. studies showed that both copolymers were successfully synthesized. It could be seen that both types of copolymer were good VI improvers with the VI values for the SNS system being generally higher than those obtained for the SAS system. Anti-wear testing results showed lower amounts of wear for both polymeric additives compared to that of a commercial lubricant product under mild wear conditions. ESCA and SEM studies were carried out to differentiate between the mechanisms for these additives under lubrication test conditions. ESCA indicated that both synthesized additives exhibited superior anti-wear properties under boundary lubrication conditions. SEM examinations testified to the fact that more chemisorption occurred in the case of the SAS additive.

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