SHORT COMMUNICATIONS

Tribological Polymerization of 2-Dibutylamino-1,3,5-Triazine-4,6-dithiol on Iron Wire during Drawing

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Tribological surface treatment makes possible the unification of processing and surface treatment of metal and lessens the requirement for metal processing. Tribological reactions of organic compounds with solid substances have been studied. Taubmann¹ and Momose² report mechanochemical polymerization to occur by milling inorganic substances in monomers. Mori and Tamai³ found vibromilled aluminum and silica powders to be effective as anionic initiators for the polymerization of vinyl acetate, styrene, methylmethacrylate, and acrylonitrile but not iron powders. They⁴ describe reactions of butylbromide with aluminum under vibromilling to give a polymerized material on aluminum powders. Such treatment is not always effective for improving general metal surfaces such as plates, wires and blocks with organic compounds since milling for long periods is required. The present authors directed attention to these studies to determine how exoelectrons are generated during and after substance processing.

In this study, 2-dibutylamino-1,3,5-triazine-4,6-dithiol was found to polymerize itself during wire drawing to give a linear polymer

on wire surfaces and to react with double-bond compounds during wire drawing to give a network polymer on a surface.

EXPERIMENTAL

2-Dibutylamino-1,3,5-triazine-4,6-dithiol (DB, mp 140°C) and triallyl isocyanurate (TAIC mp 24°C) were obtained commercially. Steel wire (JIS-AWRH82: Fe, over 98.51%, C, 0.83%, Si, 0.25%; Mn, 0.45%; P, below 0.03%; S, below 0.03%) was also purchased. Each wire sample was immersed for 5 min at 20°C in 1%-HCl aqueous solution and then 1%-NaOH aqueous solution and washed with methanol and dried in dry air (oxide film: about 10 nm).

Steel wire samples (1.43 ϕ m) pretreated above were drawn from a starting diameter of 1.43 mm to a final diameter of 1.30 mm in 2 passes by a dry drawing machine with a die box containing DB or a mixture of DB and TAIC. Drawing tests were conducted using DB and a mixture of DB and TAIC (1/1 molar ratio) as lubricants in normal production lines. The dies for drawing steel wire were standard

tungsten carbide dies.

Molecular weight and distribution were determined by gel permeation chromatography (GPC, Shimadzu GPC SWRH82A) using tetrahydrofuran (THF) sample solutions prepared by immersing drawn wires in THF for 30 min at 30°C and Showadex GPC columns (KF-802, 804, and 805; exclusion limited molecular weight, 5×10^5). A UV detector (254 nm) was used to detect organic compounds.

FT-IR spectra were measured using a Nippon Denshi FT-IR, IR-5500 (Nippon Denshi Co., Ltd.) according to the ATR method. ESCA spectra were obtained at a base pressure of 10^{-9} Torr on an X-ray photoelectron spectrometer (ESCA Lab-5, VG Scientific Co., Ltd.). A take-off angle of 35° was used with Mg-K α X-ray as the excitation source (23500 eV). AES spectra were obtained at a base pressure of 10^{-7} Torr on an Auger electron spectrometer (AES: JEOL; JAMP-10S). A take-off angle of 0° was used with Mg-K α X-ray as the excitation source (23500 eV). The etching rate by Ar $^{+}$ was 18 nm min $^{-1}$.

RESULTS AND DISCUSSION

Polymerization during Steel Wire Drawing

Metals assume activated surfaces during processing such as drawing, cutting, drilling, and rolling. This activity decreases rapidly in air. Active surfaces may cause organic compounds to change.⁵⁻⁷ Through the die box, steel wires were drawn in the presence of DB and a mixture of DB and TAIC as lubricants at various drawing rates. Figure 1 shows the GPC patterns of THF solutions obtained by extraction of the wires drawn using only DB and a mixture of DB and TAIC as lubricants; no stearic-type lubricants were used. After drawn, the wires were kept for 12 hours at room temperature. Six cut wires (10 cm in length) were immersed in THF (20 ml) and organic products adhering to the wire surfaces were dissolved in THF. Using the THF solutions, GPC pattern was used to determine mo-

lecular weights and distributions of the extracted organic compounds. By drawing as shown in Figure 1 (No. 1), DB monomer was polymerized on wire surfaces. Molecular and polymer weights increased with the drawing rate. At low drawing rate (b, 10 m min $^{-1}$), these parameters were small but increased at a high drawing rate (d, 50 m min $^{-1}$) markedly. The polymer films contained DB and DB oligomers as well as the DB polymer. The coefficients of the UV adsorption of DB (ϵ , 1.7×10^4 mol l $^{-1}$) and DB disulfide polymer (ϵ , 1.9×10^4 mol l $^{-1}$) at 254 nm⁸ showed the amount of unreacted DB to be considerably smaller than that of a polymer. The treated wire surfaces after immersion in methanol had only DB polymer films with molecular weights of about 3000 to 200000. Increased drawing rates caused wire surface temperature to increase⁹⁻¹³ as well as molecular weight and polymer weight to increase. Tribological poly-

Figure 1. GPC patterns of polymers formed on steel wire during drawing. (a) DB, no drawing; (b) DB, drawing rate 10 m min $^{-1}$; (c) DB, drawing rate 30 m min $^{-1}$; (d) DB, drawing rate 50 m min $^{-1}$; (e) washed sample; (d) with methanol; (f) DB + TAIC, drawing rate 50 m min $^{-1}$.

merization appears to run to completion instantly. No differences in molecular weight due to standing time, 10 min and 24 hours, after drawing could be detected. A mixture of DB and TAIC was also used as a lubricant in the drawing of iron wires at a drawing rate of 50 m min⁻¹, the maximum rate in the drawing test. GPC patterns indicated the formed film to contain DB, TAIC, and their polymers as shown in Figure 1 (No. 2). The intensity of UV adsorption of the polymer in the mixture was low, compared with that in DB. Thus possibly, a polymer insoluble in THF may form on wire during drawing. Both DB and TAIC may react with each other to form three dimensional organic film on wires during drawing.

Polymer film thickness on treated wires was determined based on AES as shown in Figure 2. Measurements were conducted after immersing the samples in methanol and removing

monomers. Oxide film thickness on original wire surfaces was about 10 nm. When DB was used as lubricant at a drawing rate of 50 m min⁻¹, thickness of the polymer film on the wires was about 180 nm. THF insoluble film prepared using the mixture of DB and TAIC was about 225 nm in organic film thickness. Thickness was determined as the point of intersection on the curves of carbon and iron atom content. Polymers are formed during drawing and thus organic film on iron wires should generally be thick. Organic film thickness may improve the surface properties of wire.

Chemical Structures of Polymer Films

To elucidate the chemical structures of polymer films, FT-IR spectrum measurements were made for treated wires. Steel wire surfaces treated by DB during drawing showed essentially the same FT-IR spectral patterns as

Figure 2. Changes in component atoms of wire surfaces after drawing at 50 m min⁻¹ in the presence of DB and a mixture of DB and TAIC.

Figure 3. Polymerization of DB and a mixture of DB and TAIC on steel wires during drawing.

authentic DB disulfide polymer¹⁴ prepared separately although the spectra differed from that of DB. The sample after immersion in THF showed no absorption in the FT-IR spectrum. DB treated wires thus shed all organic films by THF immersion. Before immersion, they were covered with a linear polymer. Steel wires treated with a mixture of DB and TAIC during drawing showed clear IR spectrum patterns even though the samples had been extracted with THF. An absorption peak due to CO stretching vibration at 1715 cm^{-1} (TAIC), C=C bond at 1635 cm^{-1} (TAIC), C=N bond at 1559 cm^{-1} , and 1525 cm^{-1} (DB) was seen. Decrease in absorption due to C=C bonds in TAIC and

—NHCS-group (1601 cm^{-1}) in DB suggests the formation of monosulfide groups.⁸ Only TAIC treated wire showed no adsorption peaks in FT-IR spectra following THF immersion. TAIC and DB in combination gave an insoluble polymer film by reaction of C=C bonds in TAIC with the —NHCS-group in DB. To further elucidate the chemical structure of a polymer on treated wire, ESCA spectra were measured for samples extracted with methanol. Table I show the results of electron spectra in ESCA wide scan of wire surface of the drawing at 50 m min^{-1} in the presence of DB and a mixture of lubricants and assignments of functional groups based on $\text{C}_{1\text{S}}$, $\text{N}_{1\text{S}}$, and $\text{S}_{2\text{P}}$. DB and a mixture of DB and TAIC-treated

Table I. Assignments of bonding energy for C_{1s}, N_{1s}, and S_{2p} on a narrow scan in ESCA spectra

Lubricant	Electron spectrum	Bonding energy	Bond groups	Component
		eV		%
DB	C _{1s}	286.61	-CH ₂ -, -CH ₃	63
		286.00	>C=N-	22
		287.57	>C-N<	15
	N _{1s}	398.66	-N=C<	58
		399.98	>C-N<	42
	S _{2p}	162.0, 163.1	-SS-	46
		163.4, 165.2	>C-S-	47
		168.1, 169.5	>C-SO _n -	7
DB/TAIC	C _{1s}	286.61	-CH ₂ -, -CH ₃	66
			-CH=, =CH ₂	
		287.02	>C-N<, >C=N- >C=O	34
	N _{1s}	398.62	-N=C<	23
		400.03	>C-N<	77
	S _{2p}	162.0, 163.1	-SS-, -S-	40
		163.4, 165.2	>C-S-	57
		168.1, 169.5	>C-SO _n -	3

wires showed clear peaks for C_{1s}, N_{1s}, and S_{2p}. In the former, peaks for Fe_{2p} and Fe_{3p} were observed. In the latter, none could be detected, indicating the latter to be thus more homogeneous. Assignments of peaks in the C_{1s}, N_{1s}, and S_{2p} narrow spectra of DB-treated wires showed the formation of the DB disulfide polymer. Assignments of peaks in the C_{1s}, N_{1s}, and S_{2p} narrow spectra of DB and TAIC treated wires indicated the formation of a three-dimensional polymer containing monosulfide and disulfide groups. The monosulfide group is formed by the addition of C=C bonds to TAIC and -NHCS- groups in DB.¹⁵ The disulfide group is formed by oxidative reactions between NHCS groups in DB in air.

Mechanism for Tribological Polymerization

The activity of mechanically deformed metal may be due either to (1) high temperature and pressure at the point of working contact,¹⁶ (2) newly formed nascent surfaces,¹⁷ (3) lattice

disorders,¹⁸ or (4) exoelectrons.³ The polymerization of DB on iron requires the presence of oxygen and high temperature.¹⁵ Surface temperatures of steel wires during drawing have been examined by Middiemi.⁹ For an areal reduction of 9.8% and drawing rate of 50 m min⁻¹, surface temperature reaches about 120–140°C.^{19,20} At 80°C, DB cast film was not polymerized at all on an ordinary iron plate but at 120°C in air, DB film gave a polymer film on the plate and its melting point was 140°C. DB was polymerized in the solid state. At 120°C in nitrogen atmosphere, DB film was hardly polymerized on the ordinary iron plate. Active iron and inactive plates were prepared for clarification of the effects of surface activity toward DB. The active plate was initially polished with 8 μm grain emery and degreased for 3 min at 20°C ultrasonically under methanol. The inactive plate was prepared by heating the active iron plates for 24 hours at 150°C in air oven. The surface activity of the iron

plate was a major determining factor of the polymerization activity of DB in air. The inactive and ordinary iron plates gave low polymerization activity to DB. The active iron plate imparted high polymerization activity to DB under the same conditions. The contribution of a nascent surface or exoelectrons to the polymerization of DB may be the reason for these differences. That is, polymerization may be strongly influenced by surface activity.

It thus follows that the polymerization of DB on steel wires during drawing requires oxygen, heat, and a nascent surface or exoelectrons. Thiol compounds are oxidized by oxygen in air in the presence of Fe^{+2} to give disulfides.^{17,18} Ferrous cations may be formed on a nascent iron surface during drawing. DB produces dithiyl radicals in the presence of ferrous cations and oxygen as shown in eq 1 (Fig. 1). Dithiyl radicals react with each other to give disulfide polymers as shown in eq 2. Dithiyl radicals of DB make addition to double bonds in TAIC to give three-dimensional monosulfide polymers and at the same time, coupling reactions which produce disulfide polymers, as shown in eq 3. The addition of DB to TAIC on glass and inactive iron plates left for a long time in air failed to occur for 60 min at 120°C. This would imply the formation of dithiyl radicals on a nascent surface during drawing.

In conclusion, by tribological polymerization, it should be possible to unify metal processing and surface treatment. This in turn should lead to ultimate surface treatment of

metals because it can be carried out easily in a very short time at low cost.

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