

Friction of Polymer Films. III. Migration of Lubricants

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Synopsis

The migration of the lubricant stearamide to the surface of vinylidene chloride-acrylonitrile copolymer coatings on regenerated cellulose film was studied by measuring the effect of heating the coatings on friction and critical surface tension. The surface quantity of stearamide was maximum at a heating temperature of 65°C. Above this temperature stearamide was lost from the surface. Up to 65°C the migration of lubricant obeyed first-order kinetics and the activation energy was calculated. Below 65°C diffusion to the surface appears to be the controlling process, while above 65°C evaporation from the surface is probably the controlling process.

INTRODUCTION

Earlier work¹ has shown that coatings of vinylidene chloride-acrylonitrile copolymer on regenerated cellulose films could be effectively lubricated by dissolving long-chain fatty amides in the coating solution. Upon drying, these amides appeared on the surface of the coating in amounts which increased with the chain length of the amide. It was proposed that the appearance of this surface layer of fatty amide was a result of the diffusion of the amide (molten at the temperatures used to dry the coating) to the surface of the copolymer film. The differing amounts of amide at the surface of the film according to molecular weight were a function of the compatibility of the amide with the copolymer. Subsequent work to be reported here will show that it is not necessary for the amide to be molten to migrate to the surface; this process can occur at temperatures far below the melting point of the amide. Such migration of solid lubricants through solid polymers is well known. Allan² studied the behavior of oleamide in polyethylene film. He found that oleamide continued to migrate to the surface of the cold film for several days following extrusion and considered surface activity of the oleamide in the polyethylene film as the driving force for migration. Bowers et al.³ have shown several unequivocal examples of surface activity of lubricants in polymers. Using bis(1*H*,1*H*-pentadecafluorooctyl) tetrachlorophthalate at a concentration of 1% in a film of vinylidene chloride (85%)–acrylonitrile (15%) copolymer, the coefficient of friction was reduced from 0.80 to 0.10 and the critical surface tension γ_c was reduced from 38 ~ 44 dynes/cm to 18 dynes/cm. Of great interest was

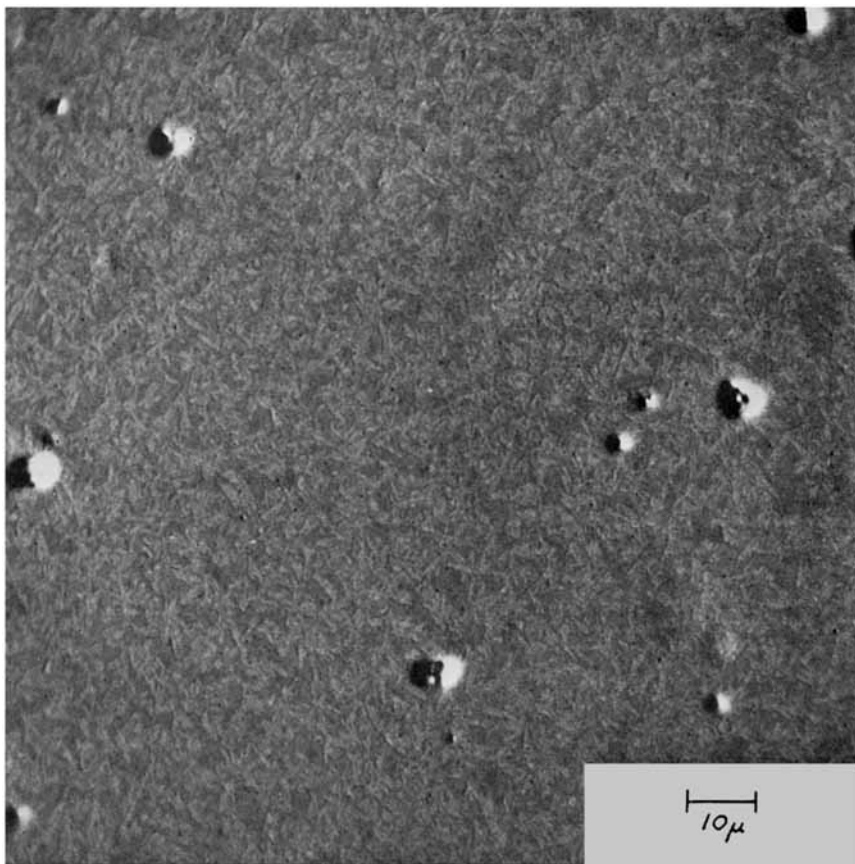


Fig. 1. Unheated copolymer film.

evidence that the lubricant layer was self-healing. Material removed by frictional sliding was replaced by lubricant diffusing from within the bulk of the polymer.

EXPERIMENTAL

The procedure for preparing the coatings and measuring coefficients of static friction and γ_c was the same as described previously.¹ The copolymer was 90% vinylidene chloride–10% acrylonitrile. The softening point of the copolymer was 140°–145°C and the glass transition temperature was 18°C measured by torsion pendulum. A drying time of 30 sec at 145°C was used to form the coating rather than the 130°C employed for the previous work. The stearamide was Eastman White Label purified by two recrystallizations from ethanol. It had a melting point of 108°C and was incorporated into the coating at the level of 2% by weight of copolymer. Coated films were subsequently heat treated by suspending them in a forced draft oven.

RESULTS

The freshly coated films were stored at room temperature (21°C) for 72 days. Periodic measurements of the coefficient of static friction μ_s and of γ_c showed no change over this period. The microscopical appearance of the film (Fig. 1) did not change. Although the crystals of stearamide are visible in Figure 1, they are not sharply defined, as though they were just beneath the surface of the copolymer rather than on it. The friction value, 0.96, for films dried at 145°C was much higher than the value of 0.35 for films dried at 130°C in previous work.¹ These findings suggest that the higher drying temperature and consequent faster drying rate do not allow sufficient time for the lubricant to diffuse to the film surface in quantity.

Effect of Heat

Coated films were heated in an oven for 1 min at temperatures from 45° to 110°C. Measurements of γ_c and friction were made on the films after they were cool and are given in Table I. These data are shown graphically in Figure 2. Heating results in an initial decrease in both μ_s and γ_c up to a temperature of 65°–70°C above which the friction and critical surface tension increase. The results are curves with pronounced minima. Microscopical observations show an increase in the amount of stearamide on the film surface, with the maximum at 65°C followed by a decrease at higher temperatures. Figure 3 shows the film heated at 45°C. The stearamide crystals are more sharply defined than in the unheated film of Figure 1.

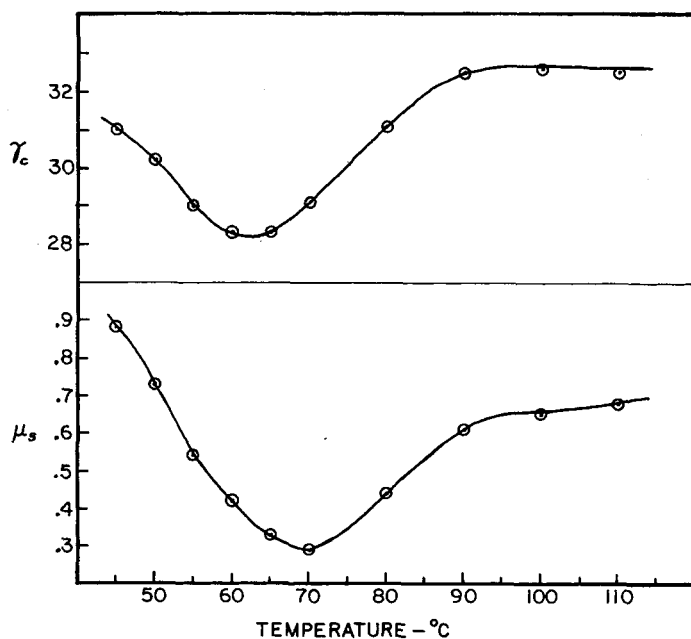


Fig. 2. Effect of heat on γ_c and static friction of copolymer coatings.

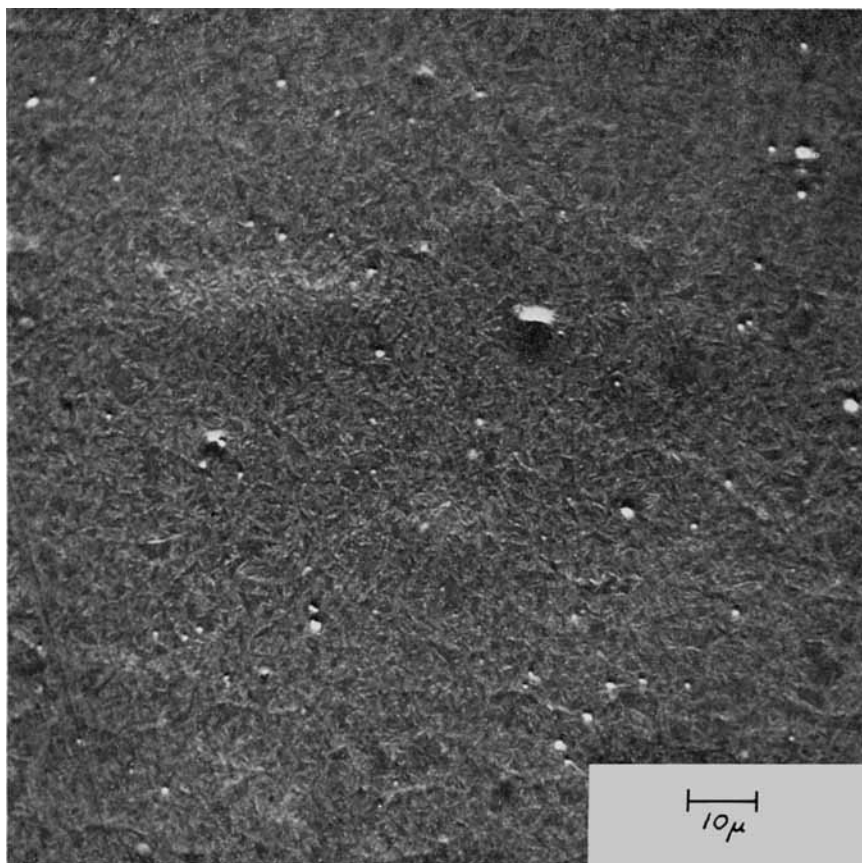


Fig. 3. Copolymer film heated at 45°C.

Figure 4 shows the film heated at 65°C completely covered with stearamide crystals. The γ_c value of 28.3 for film heated at 65°C is in good agreement with the value of 28.7 previously reported for bulk stearamide.¹ The

TABLE I
Friction and γ_c of Heated Films

Temperature, °C	μ_s	γ_c , dynes/cm
Control	0.96	33.0
45	0.88	31.0
50	0.73	30.2
55	0.54	29.0
60	0.42	28.3
65	0.33	28.3
70	0.29	29.1
80	0.44	31.1
90	0.61	32.5
100	0.65	32.6
110	0.68	32.5

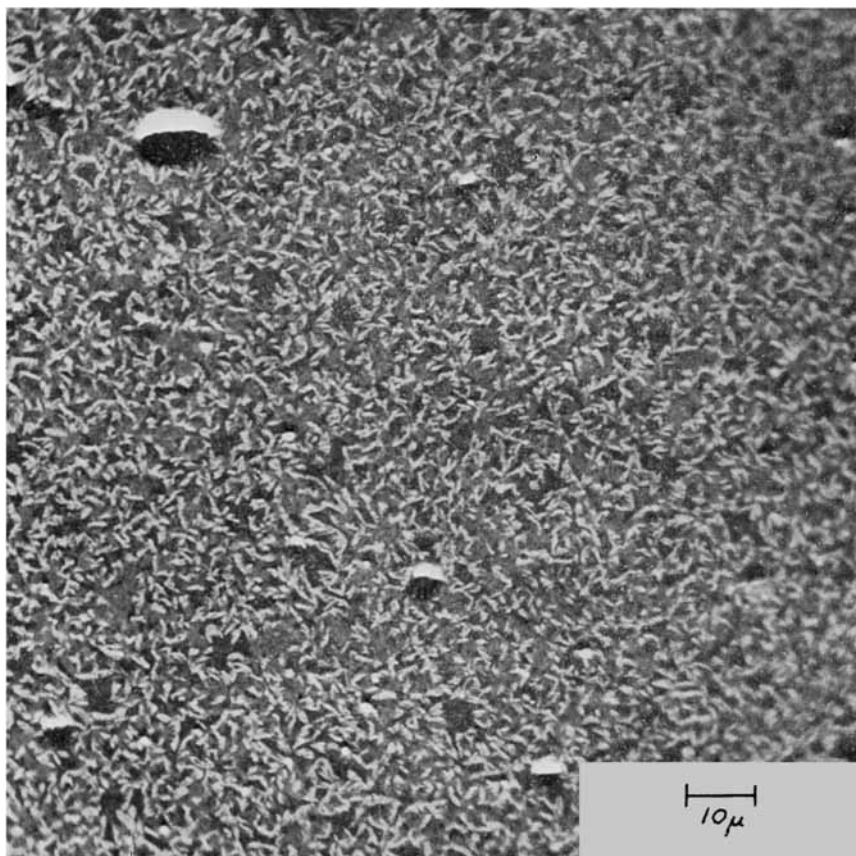


Fig. 4. Copolymer film heated at 65°C.

photomicrographs of Figures 5 and 6 show the progressive decrease in the amount of stearamide on the copolymer film surface at heating temperatures of 90° and 110°C.

Kinetics

The initial process of friction reduction was studied by heating films for various lengths of time at two temperatures, 45° and 65°C. Using μ_s as a measure of the quantity of stearamide on the film surface, the data were fitted to a first-order rate equation of the form

$$\ln (\mu_s - \mu_s^e) = \ln (\mu_s^0 - \mu_s^e) - kt \quad (1)$$

where μ_s = coefficient of static friction, μ_s^e = minimum coefficient of static friction, μ_s^0 = coefficient of static friction at zero time, t = time (min), and k = rate constant (min^{-1}).

The plot of $\mu_s - \mu_s^e$ versus t is shown in Figure 7. The data fit the equation well. Calculated rate constants are $k_1 = 0.204 \text{ min}^{-1}$ at 45°C and $k_2 = 2.172 \text{ min}^{-1}$ at 65°C. The value of μ_s^0 by extrapolation is 1.17

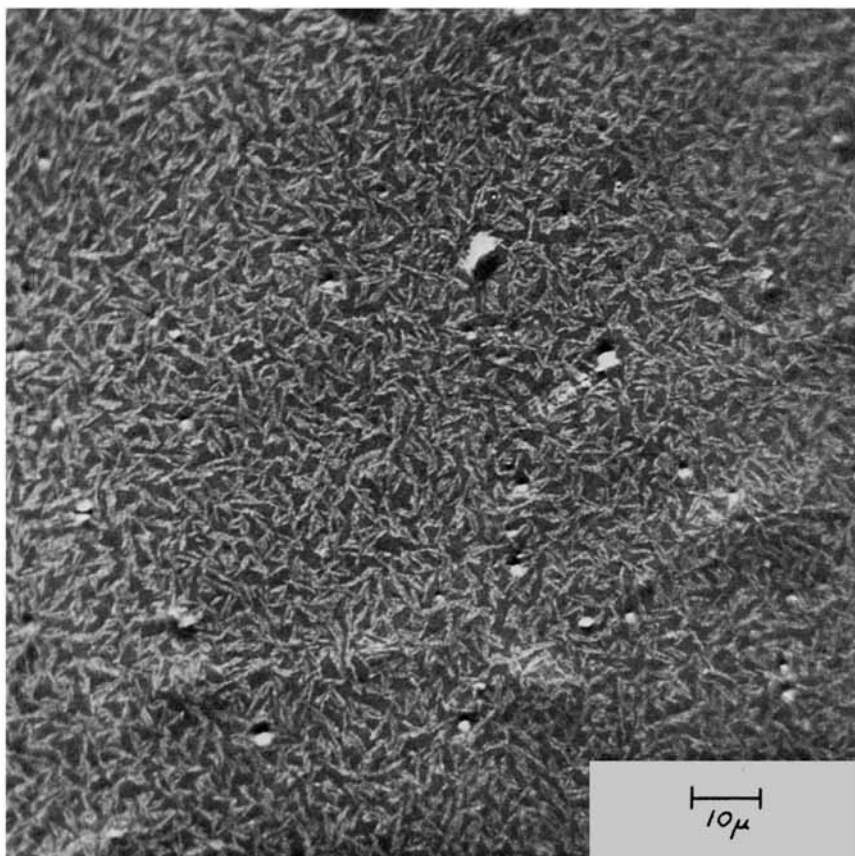


Fig. 5. Copolymer film heated at 90°C.

rather than 0.96 as measured. Implicit in eq. (1) is the assumption that the concentration of stearamide on the film surface is zero at zero time when this is, in fact, not the case. There is some amide on the film surface before heating, causing lack of agreement between the extrapolated and measured intercepts.

With the rate constants calculated at two temperatures, the activation energy ΔE can be computed from the Arrhenius equation

$$\Delta E = \frac{2.303 RT_1 T_2}{T_2 - T_1} \log \frac{k_2}{k_1} \quad (2)$$

where T = temperature ($^{\circ}\text{K}$) and R = gas constant (1.987 cal/ $^{\circ}\text{K}$ g-mole). The energy of activation calculated from eq. (2) is 25.3 kcal.

SUMMARY AND CONCLUSIONS

The migration of stearamide to the surface of copolymer coatings is remarkably temperature dependent. The process does not occur to any

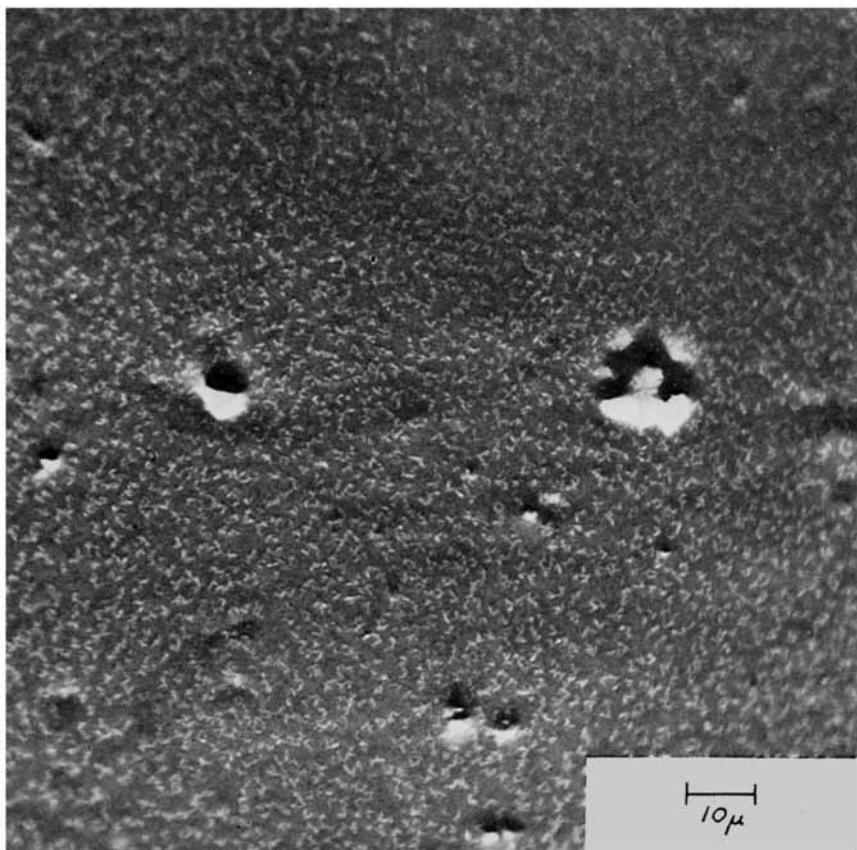


Fig. 6. Copolymer film heated at 110°C.

perceptible extent at 21°C, but is greatly accelerated by an increase to 45°C. The rate then increases tenfold for a further 20° increase in temperature. The room temperature behavior of this system is in marked contrast to the oleamide-polyethylene system where significant migration of the oleamide occurred in a short time at room temperature. The stearamide-copolymer system is also remarkable in that the optimum temperature of 65°C for migration of the amide is 43°C below the melting point of the amide and ca. 80°C below the softening point of the copolymer. The optimum temperature for migration does not appear related to T_g of the copolymer. The activation energy for the process is not unusual. It is concluded that the migration occurs in the solid state. Of interest also is the fact that stearamide undergoes a transition at 64°C which probably involves a change of the lattice spacing of the crystal.⁴ The coincidence of the transformation temperature and the temperature of maximum migration may be fortuitous.

The curves of Figure 2 indicate the presence of two competing processes. Below 65°C diffusion to the surface appears to be the controlling process.

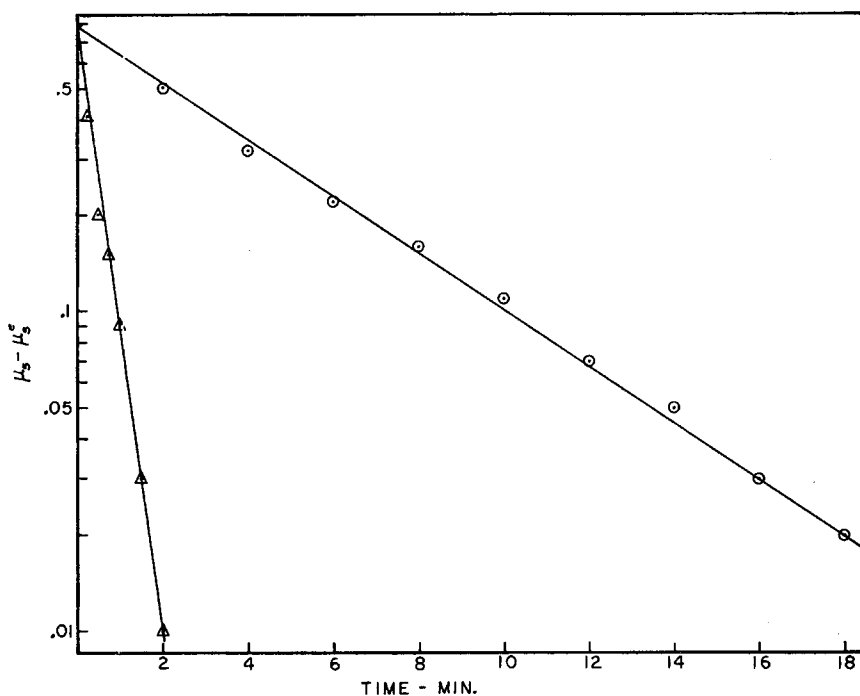


Fig. 7. Application of first-order equation to friction vs. heating time data: (\odot) 45°C; (\triangle) 65°C.

Above 65°C the rate of disappearance of stearamide from the film surface exceeds the rate of diffusion of amide to the surface, causing the friction and surface energy to rise. The mechanism of disappearance is probably evaporation. Under the treating conditions of rapidly moving hot air and large exposed surface area, significant evaporation would be expected. The heat of sublimation of stearamide is 46.8 kcal/mole, which is not extremely high.⁵ Again it is of interest that the disappearance of the amide is predominant only above its transformation temperature.

Another possible explanation for the disappearance of amide from the film surface is that the amide may become soluble in the copolymer at elevated temperatures and diffuse into the copolymer. The experimental data do not distinguish between the two possibilities, however.

References

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