Friction of Polymer Films.   I.   Lubrication

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Synopsis

   The behavior of several long chain fatty lubricants in thin films of vinylidene chloride–acrylonitrile copolymer and the nature of the lubricated polymer surfaces were studied by means of frictional measurements, critical surface tension of wetting, and light microscopy.   The surfaces of the bulk lubricants were also characterized by wetting studies.   The critical surface tension of wetting parameter was found to be both a means of characterizing the configuration of the lubricant layer and a measure of the extent to which the polymer surface was covered by the lubricant.   There was no evidence of orientation of the lubricant layer on the polymer surface and no evidence of plasticization of the polymer by the lubricant.   All lubricants studied appeared in the bulk state at the polymer surface in quantities related to the chain length and chemical constitution of the lubricant.   Correlations were observed between the coefficient of static friction of the polymer film and its critical surface tension of wetting.   Solid fatty amides having chain lengths of eighteen carbon atoms or greater were found to be effective lubricants for the polymer studied.   The lubricating action of these fatty materials was explained in terms of their low surface energies and high structural strengths when in the bulk crystalline state.

I. INTRODUCTION

   Regenerated cellulose film coated with vinylidene chloride–acrylonitrile copolymer to confer moistureproofness is extensively used as a packaging material.   The surface of this polymer often exhibits an undesirably high friction against itself, and it is desirable to provide lubrication for the film surface to obtain satisfactory packaging machine performance.

   It is generally agreed that polar, long-chain fatty compounds are excellent lubricants for metals because of their ability to form close-packed, strongly adsorbed, oriented monolayers on these substrates.   Boundary friction values of 0.10 and often as low as 0.05 are frequently encountered with lubricated metals.[1]   Polar fatty compounds are not as effective, however, for polymer lubrication.   Bowers, Clinton, and Zisman,[2] using a variety of lubricants, were able to achieve a static coefficient of friction of only 0.50 for nylon on nylon compared to the unlubricated value of 0.75.   They attributed the poor lubrication to the lack of polarity of the polymer which precluded adsorbed oriented monolayer formation.

   Pascoe[3] has explained the ineffectiveness of lubricants on polymers by postulating that the shear strengths of the lubricant layer and the polymer are not appreciably different and hence, only small decreases in friction are

observed with lubrication. Rubenstein[4] has theorized that the lubricant may act as a plasticizer for the polymer. While the lubricant may reduce the shear term S at the sliding interface, it may also reduce the hardness p of the polymer so that the S/p ratio remains constant or may even increase. Thus the decrease in friction due to reduced shear strength may be offset and even exceeded by the increase in friction due to softening.

The foregoing theories were based primarily on results obtained with liquid lubricants or solutions of solid lubricants in inert liquids. Fort and Olsen[5] and Fort[6] have reported results on the friction of several different polymers lubricated with a variety of fatty compounds. Their results with liquid lubricants agreed with previous work. The coefficient of friction of rayon was reduced from 0.72 to only 0.60 with oleic acid. When solid lubricants were applied from solvent and the solvent allowed to evaporate, much larger decreases in the coefficient of friction were observed. Reductions from 0.72 to 0.28 for stearic acid and 0.72 to 0.20 for octadecylamine were seen in the case of rayon. To explain the failure of these lubricants to reduce the friction of polymers to values as low as those obtained with lubricated metals, they proposed that the lubricant was very weakly adsorbed on the polymer surface. They did not observe evidence of plasticization with either solid or liquid lubricants.

Evidence in our laboratory also indicated that satisfactory lubrication of polymers could be achieved with solid, polar, fatty compounds. A study was initiated to determine the physical nature of the lubricated polymer surface and to define the mechanism of lubrication.

II. EXPERIMENTAL

Coatings of vinylidene chloride–acrylonitrile copolymer were applied to regenerated cellulose film by spreading a thin layer of polymer solution on the film and drying it in a hot air oven. The lubricants to be studied were dissolved in the polymer solution prior to coating the cellulose film.
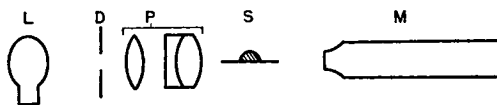

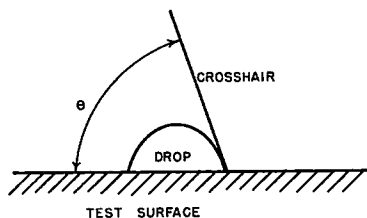Fig. 1. Schematic of contact angle goniometer.

Fig. 2. Geometry of contact angle measurement.

All lubricants were used at the concentration of 2% by weight of the polymer. With the exception of octadecylamine and oleamide, all lubricants were purified by two recrystallizations from ethanol. By adjusting the concentration of polymer in the solution, thin coatings could be obtained. Coatings of equal thickness were used for studies of differences between lubricants. A drying time of 30 sec. at 130°C. was sufficient to remove all solvent from the coatings. Layers of bulk, crystalline fatty compounds were prepared for study by melting a small amount on a glass slide to form a thin film and quickly chilling the slide.

The surface character of the lubricated coatings was evaluated by using the wetting methods of Zisman[7] to determine the critical surface tension
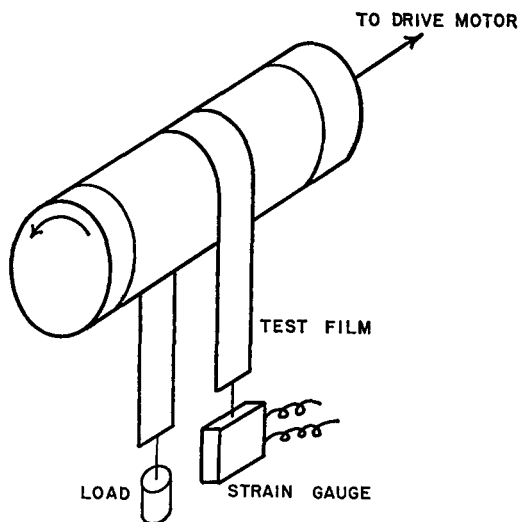

Fig. 3. Capstan friction machine for films.

γ_c of wetting. The test liquids were mixtures of dipropylene glycol and water which provided a graded series of surface tension liquids from 35.6 dynes/cm. (85% dipropylene glycol) to 62.2 dynes/cm. (2% dipropylene glycol). Liquid surface tensions were measured by the ring method. The choice of liquids was restricted to aqueous solutions because organic liquids had undesirable solvent effects on the polymer. Contact angles were measured with an optical goniometer of our own design shown schematically in Figure 1. The lamp, L, illuminates a crosshair mounted over an opening in the circular, revolving disk, D, which is graduated in degrees. The lens system, P, projects an image of the crosshair into the plane of the specimen at S. The 10-power microscope, M, permits viewing the specimen and crosshair image superimposed on one another. The test liquid was applied to the surface under study from a capillary tube to form a drop which was increased in size until the contact angle became constant. This angle was then recorded as the advancing contact angle. The geometry of

measuring the contact angle, θ, is shown in Figure 2.   The precision of the method is approximately ±0.3 dynes/cm.

The physical configuration of the polymer surface and the disposition of the lubricant were studied microscopically by using the metallization method of Owens.[8] With this method, even a monolayer of fatty substance can be made visible.

Forces of friction of the polymer film on itself were determined with a modification of the capstan machine described by Fort and Olsen,[5] and coefficients of friction were calculated by the familiar belt equation as given by these authors.   The apparatus is shown schematically in Figure 3. The drum, connected to a variable speed drive, is covered with the film under test.   A second strip of test film is hung over the drum with one end attached to a strain gauge, and a pretensioning weight is fastened to the free end.   When the drum is rotated, the frictional force between the films is registered by the strain gauge.   There is sufficient elasticity in the system to allow stick-slip motion to occur.   Static coefficients of friction were calculated from the average of five successive peaks in the stick-slip motion. For this work a Sanborn recorder was used to display the strain gauge output.   The pretensioning load was 30 g. and the peripheral speed of drum rotation was 0.01 cm./sec.   A precision of ±0.02 friction unit was obtained in practice.

III. RESULTS

Bulk Lubricants

Zisman et al.[7] have shown that an excellent approach to measuring the surface free energy of a solid may be had by determining the surface tension required of a liquid in order that it spread or exhibit zero contact angle on the solid.   This value of surface tension is termed the critical surface tension, γ_c, and is determined experimentally by measuring the contact angles of several liquids of different surface tension with the test solid. They have shown that a rectilinear plot of liquid surface tension versus cosine of the contact angle, θ, with the test solid gives a straight line in the case of an homologous series of liquids.   The intercept of this line with the surface tension axis when extrapolated to $\cos\theta = 1$ (zero contact angle) is the value of γ_c.   In the case of dipropylene glycol solutions, a straight line was obtained only with a log–log plot.   This difference may be due to the lack of homology or to the use of a binary liquid system.

Excellent agreement between values of γ_c determined in the above manner and those appearing in the literature for several reference substances were obtained.   Table I shows some literature values[7] along with some experimental values of γ_c for various surfaces tested.

The critical surface tension value for the methyl group in crystalline configuration is 20–22 dynes/cm., and the value for a surface composed of methylene groups is 31 dynes/cm. from Table I.   It was expected that bulk, crystalline paraffin wax would present a surface composed partly

TABLE I
Critical Surface Tension of Various Solids

Surface	γ_c, dynes/cm.	
	Literature	Experimental
—CH$_3$ (crystal)	20–22	—
—CH$_3$ (monolayer)	22–24	—
—CH$_2$—	31	—
Polyethylene	31	31.5
Polyvinylidene chloride	40	—
Polyvinylidene chloride–acrylonitrile copolymer	—	38.0[a]
Polyethylene terephthalate	43	42.5
Bulk paraffin wax (m.p. 51°C.)	—	27.2
Bulk behenic acid (C$_{22}$)	—	29.0
Bulk lauramide (C$_{12}$)	—	29.4
Bulk myristamide (C$_{14}$)	—	28.8
Bulk palmitamide (C$_{16}$)	—	29.1
Bulk stearamide (C$_{18}$)	—	28.7
Bulk behenamide (C$_{22}$)	—	29.0

[a] Cleaned by rinsing with carbon tetrachloride.

of methylene groups and partly of methyl groups and exhibit a γ_c value intermediate between the values for each type of group. Experimentally a value of 27.2 dynes/cm. was found. Experimental measurements on bulk, crystalline fatty acids and amides yielded γ_c values of approximately 29 dynes/cm. It appears that the polar group in a bulk fatty compound contributes little to the total surface energy. Within experimental error, no differences in the γ_c values of the fatty material were noted due to chain length over the range C$_{12}$ to C$_{22}$. No conclusions concerning the surface constitution of the bulk fatty compounds studied can be drawn, however, the experimental γ_c values for these materials are quite useful in determining the nature of a polymer surface lubricated with them.

Lubricated Polymer Films

The fatty compounds described above along with several others were incorporated into polymer coatings on cellulose film in the manner previously cited. Values for γ_c and the coefficient of static friction were obtained for each film, and photomicrographs were made of the film surfaces. The results of the surface energy and friction measurements are shown in Table II.

There is a definite correlation between the γ_c value and the coefficient of static friction μ_s. This correlation is shown graphically in Figure 4 and follows the form:

$$\ln \mu_s = n\gamma_c + k$$

where n and k are constants equal to 0.28 and -9.9, respectively. The lowest γ_c value obtained for this series of lubricated films was 28.5 dynes/

TABLE II
Critical Surface Tension and Static Friction for Various Lubricated Film Surfaces

Film	γ_c, dynes/cm.	μ_s,
Vinylidene chloride–acrylonitrile copolymer	34.2[a]	0.76
Copolymer + lauramide (C_{12})	34.2	0.71
Copolymer + myristamide (C_{14})	33.5	0.61
Copolymer + palmitamide (C_{16})	33.0	0.52
Copolymer + stearamide (C_{18})	32.0	0.35
Copolymer + behenamide (C_{22})	28.5	0.15
Copolymer + oleamide (C_{18} unsat.)	33.5	0.69
Copolymer + octadecylamine (C_{18})	30.5	0.24
Copolymer + behenic acid (C_{22})	32.5	0.47

[a] Polymer surface not cleaned prior to measurement.

cm. for the film containing behenamide; this value agreed closely with the γ_c value for the bulk amide. In no case were γ_c values for lubricated films found which were lower than the values for the bulk lubricant.

For the homologous series of fatty amides, a correlation between the γ_c and μ_s measurements and the molecular weight of the amide was noted. The surface free energy and the coefficient of static friction decreased as the molecular weight increased. In the case of lauramide, a C_{12} fatty amide, identical γ_c values were found for a film containing this lubricant and one containing no lubricant.

Since this series of fatty amides exhibited similar bulk values of γ_c, the evidence strongly suggested that the amount of lubricant on the surface of the polymer film was varying with the molecular weight of the lubricant.
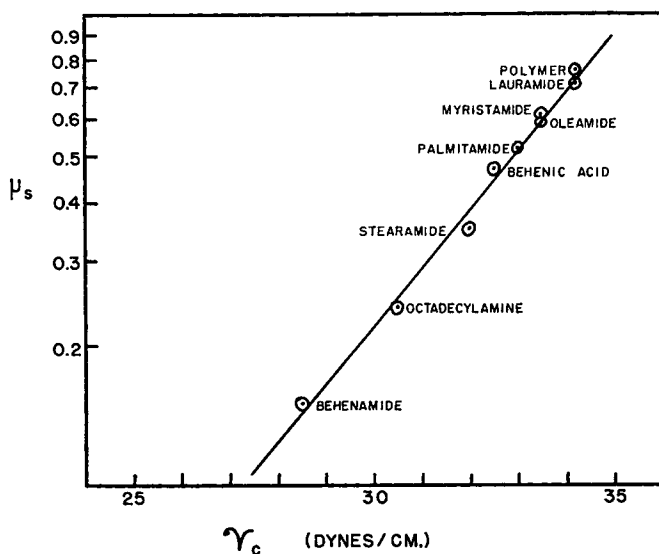

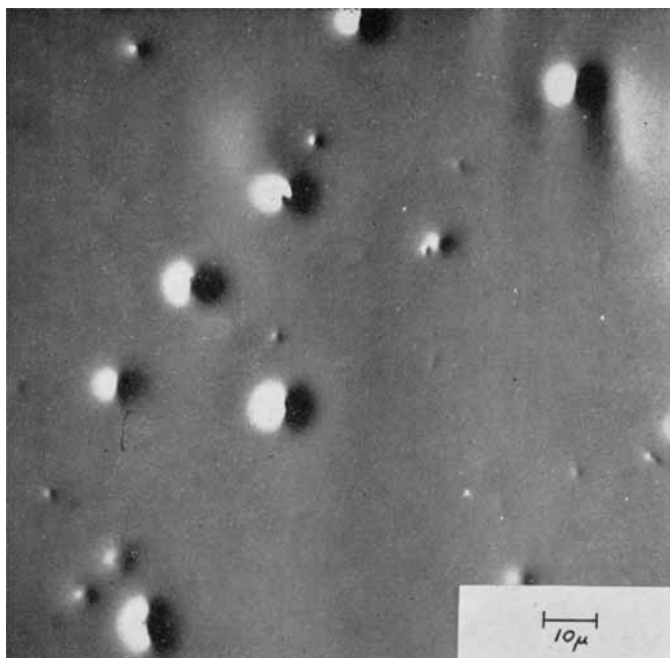Fig. 4. Static friction vs. critical surface tension for lubricated films.

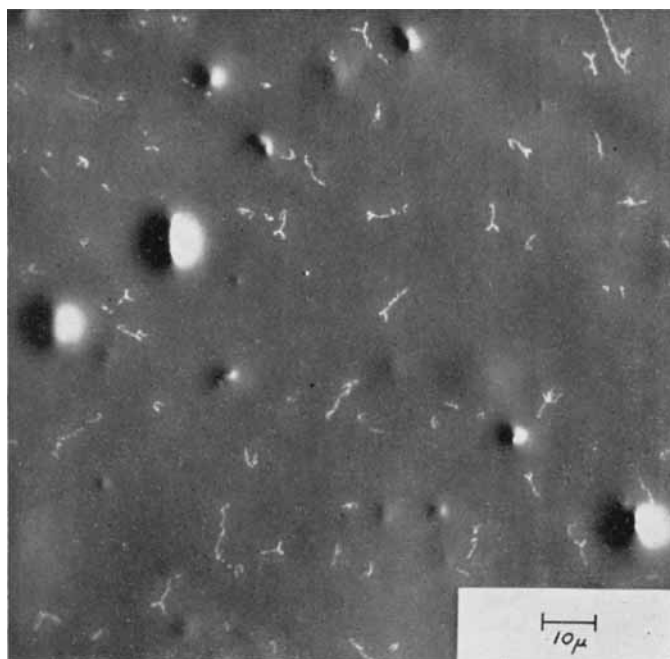Fig. 5. Polymer film containing lauramide.

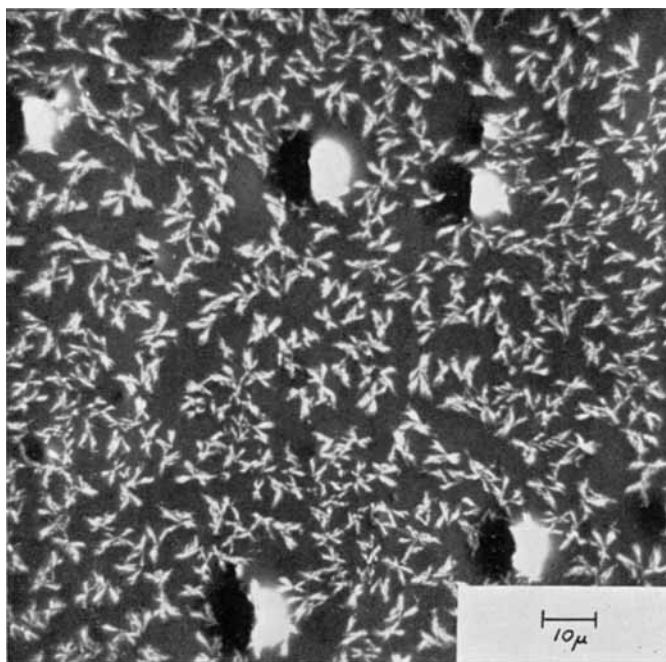Fig. 6. Polymer film containing myristamide.
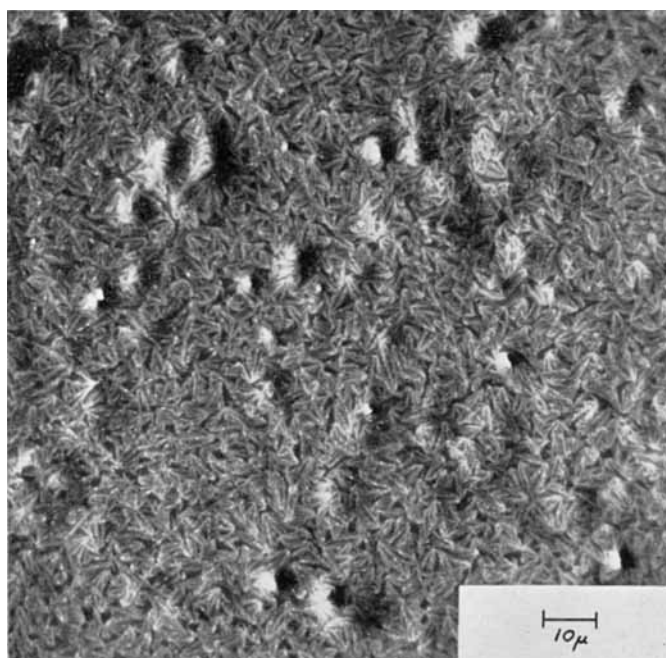
Fig. 7. Polymer film containing palmitamide.

Fig. 8. Polymer film containing stearamide.

Photomicrographs showed that this was the case.   The film containing lauramide had no amide visible on its surface, as shown in Figure 5.   Figure 6 shows a few crystals of myristamide scattered about the surface of the polymer, and Figures 7 and 8 show the progressive increase in the quantity of lubricant at the surface when palmitamide and stearamide are used. The large spherical protrusions in the photomicrographs are particles of finely ground clay incorporated into the polymer to prevent matting of the films.

IV. SUMMARY AND CONCLUSIONS

No conclusions can be drawn about the surface constitution of layers of bulk, fatty lubricants from wetting studies, however, values of critical surface tension obtained from these studies are characteristic of the bulk state and can be used to distinguish this configuration from other possible ones when these lubricants are used on polymer surfaces.

When the fatty amide lubricants were incorporated into a solution of vinylidene chloride–acrylonitrile copolymer which was subsequently formed into a thin coating on cellulose film, the lubricants appeared at the surface of the polymer in quantities which increased as the molecular weight of the lubricant increased.   The lowest value of critical surface tension found for a lubricated polymer film was the same as the value for the bulk lubricant.   This evidence indicates that the lubricants are present on the polymer surface in the bulk crystalline configuration.

Photomicrographs of the lubricated polymer surfaces indicated that the surfaces were incompletely covered with lubricant when low molecular weight lubricants were used.   Critical surface tension measurements of these surfaces yielded values intermediate between those for bulk lubricant and unlubricated polymer.   There was no evidence for the presence of an oriented monolayer of lubricant on the exposed polymer surface between the crystals of lubricant.   If this were the case, a γ_c value lower than that for the bulk lubricant would be expected.   The progressive decrease in γ_c for an increasing homologous series of amides appears to be a measure of the extent to which the polymer surface is covered with the amide.

Complete surface coverage by lubricant and effective lubrication were observed when the lubricant was a solid fatty amide of 22 carbons chain length.   The effectiveness of lubrication decreased as the chain length of the lubricant decreased.   Fatty acids and unsaturated fatty amides were not as effective in providing lubrication for the polymer system under study.   There was no evidence of plasticization of the polymer by the lubricant.   The C_{12} fatty amide which was completely retained within the bulk of the polymer did not raise the coefficient of static friction above that of the unlubricated polymer.   In the case of a plasticizing action by the lubricant, an increase in the coefficient would be expected.

The following hypothesis is offered to explain the mechanism of lubrication of the vinylidene chloride–acrylonitrile copolymer used in this investi-

gation. At the temperatures used to dry the polymer–lubricant solution, the lubricant is molten. In this state it diffuses to the surface of the polymer film in quantities sufficient to crystallize when the film is cooled. When equal weights of different lubricants are used in the polymer, the quantity of lubricant which diffuses to the surface is dependent on the molecular weight and, to some extent, on the chemical composition of the lubricant. It is quite probable that the reason for this behavior can be explained in terms of the compatibility of the lubricant molecule with the polymer molecule. Short-chain lubricants are more compatible with the polymer system and are, for the most part, included into the polymer structure rather than exuded to the surface. A composite surface of randomly oriented lubricant crystals and exposed polymer is formed, with the proportions of each dependent on the nature of lubricant. When the surface of the polymer is completely covered with lubricant, a low energy surface is formed which has low adhesion and consequently a low coefficient of friction. Although an adsorbed monolayer is not formed, the close packing of the molecules in the crystalline lubricant layer confers structural strength and enables the layer to support large loads without disruption. The relative ineffectiveness of the common liquid lubricants on polymers is also explained by this mechanism, since these liquids can neither form an adsorbed monolayer nor crystallize on the polymer surface.

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Résumé

On a étudié le comportement de plusieurs lubrifiants gras à longues chaînes dans des films de copolymères de chlorure de vinylidène et d'acrylonitrile ainsi que la nature des surfaces du polymère lubréfiées au moyen de mesures de friction, de tension superficielle critique de mouillage et microscopie à lumière incidente. Les surfaces de lubréfiants bruts ont également été caractérisés par des études de mouillage. On a trouvé que la tension superficielle de mouillage permet de déterminer la configuration de la couche de lubréfiant et est une mesure de l'étendue de la surface de polymère recouverte par le lubréfiant. Il n'y a pas de preuve d'une orientation de la couche de lubréfiant sur la surface polymérique ni d'une plastification du polymère par le lubréfiant. Tous les lubréfiants étudiés se présentent en masse sur las surface du polymère, en quantités proportionnelles à la longueur de la chaîne et à la constitution chimique du lubréfiant. On a observé des corrélations entre le coefficient de friction statique du film polymérique et sa tension

superficielle critique de mouillage. Des amides grasses solides dont les chaînes comportent dix-huit atomes de carbone ou plus apparaissent comme des lubréfiants efficaces pour les polymères étudiés. L'action lubréfiante de ces matières grasses est expliquée par des considérations sur leurs faibles énergies de surface et leurs tensions structurelles élevées lorsqu'ils sont à l'état cristallin brut.

Zusammenfassung

Das Verhalten einiger langkettiger Schmiermittel auf Fettbasis in dünnen Vinylidenchlorid-Acrylnitril-Copolymerfilmen und die Natur der geschmierten Polymeroberfläche wurden durch Reibungsmessungen, Bestimmung der kritischen Benetzungsoberflächenspannung und Lichtmikroskopie untersucht. Ausserdem wurde die Oberfläche des Schmiermittels allein durch Benetzungsuntersuchungen charakterisiert. Die kritische Benetzungsoberflächenspannung kann sowohl zur Charakterisierung der Konfiguration der Schmiermittelschicht als auch als Mass für die Bedeckung der Polymeroberfläche durch das Schmiermittel dienen. Es konnte weder eine Orientierung der Schmiermittelschicht auf der Polymeroberfläche noch eine Weichmacherwirkung des Schmiermittels auf das Polymere nachgewiesen werden. Alle untersuchten Schmiermittel liegen an der Polymeroberfläche in makroskopischer Phase und in von der Kettenlänge und der chemischen Konstitution des Schmiermittels abhängigen Mengen vor. Der statische Reibungskoeffizient des Polymerfilmes steht zu dessen kritischer Benetzungsoberflächenspannung in Beziehung. Feste Fettsäureamide mit einer Kettenlänge von achtzehn oder mehr Kohlenstoffatomen sind wirksame Schmiermittel für die untersuchten Polymeren. Die Schmierwirkung dieser fettartigen Stoffe wird durch ihre niedrige Oberflächenenergie und hohe Strukturfestigkeit im reinen kristallinen Zustand erklärt.

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