



# Migratory Internal Lubrication of Thermoplastic Resins

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*Partial alloys of high molecular weight thermoplastic resins with polysiloxanes were prepared and evaluated for wear, friction, pressure velocity limits, and mechanical properties. In particular, polyamide, polymethylene oxide, polycarbonate, and polystyrene alloys were considered. The alloys were also prepared as composites with PTFE and glass-fiber. In all cases, enhanced wear and frictional properties were observed. For a polyamide wiped clean of polysiloxane, contact-angle experiments indicate that a new layer of boundary lubricant may be formed within thirty-six hours. Polymethylene oxide specimens periodically wiped clean of lubricant exhibited wear rates identical to freshly prepared specimens.*

## INTRODUCTION

Migratory internally lubricated thermoplastics are blends of a thermoplastic resin with a lower molecular weight material. The lower molecular weight material is selected both for its ability to behave as a boundary lubricant and a limited compatibility with the thermoplastic resin. The lower molecular weight material moves to the surface by two processes—diffusion by random molecular movement and exclusion from the matrix due to limited compatibility. The net result is the continual generation of a film which behaves as a boundary lubricant. Early work with materials of this general description was limited to the addition of amphiphatic fatty acid amides to polyethylene (1, 2). These materials are incorporated in relatively low percentages and demonstrate severely limited utility in bearing applications. In order to generate a low-friction surface under practical conditions, 30 molecular layers of

lubricant are required (3). The layer of boundary lubricant initially formed comprises the bulk of incorporated lubricant. Initially, regeneration is swift but drops off and fails entirely after a brief period of time.

Preliminary reports have indicated that low-friction surfaces may also be generated on thermoplastic polymers by preparing partial alloys of the high molecular weight resins with low molecular weight polymeric lubricants. Polystyrene (4), polyamides (5), and polymethylene oxides (5) have been alloyed with polysiloxanes. The compositions appear to maintain low coefficients of friction and low wear rates over longer periods of time than the amphiphatic systems. This investigation was initiated in order to explore the resin systems to which polysiloxane alloying may be extended, as well as to examine the parameters concerned with the appearance of the polysiloxane on the surface of the polymer. With the ultimate goal of producing thermoplastic materials with extremely low wear rates, the resin-siloxane alloys were prepared as composites with polytetrafluoroethylene (PTFE) and glass-fiber reinforcement.

## RESULTS

Experimental details of wear testing have been discussed in previous publications (5, 6). Wear is determined on a thrust washer (face ID 0.900 in–0.905 in, face OD 1.120 in–1.125 in) operating at 50 ft/min under 40 psi load and mating against 12 rms SAE 1040 steel. It has been found that in cases where PV limit is not approached, wear is relatively independent of velocity and loading. Wear (“K” factor) appears as a dimensioned constant  $10^{-10}$  in<sup>3</sup> min/ft/lb/hr since the term for hardness has been omitted. Limiting pressure velocity (LPV) is determined on half-journal bearings with 1-in inner diameter, 0.060-in wall 1 inch in length. Specimens are step-loaded at various test velocities (10 ft/min, 100 ft/min, and 1000 ft/min). The

last loading where the specimen maintains equilibrium without demonstrating increased torque or temperatures is designated the limiting pressure velocity (LPV) for that specific velocity.

Wear and LPV data for a series of neat thermoplastic resins with the addition of polydimethylsiloxane having an Mn of 40,000 is tabulated in Table 1. Incorporation of the silicone resulted in a 55 percent reduction in wear for the polyacetal copolymer and an 80 percent reduction in wear for nylon 6/6 (RV 58). At low velocities, the increase in LPV is modest, but at higher test velocities, substantial improvements (up to 1,000 percent) are observed. This can be attributed to the ability of the silicone to maintain boundary lubrication at high velocities and its relative inability to withstand high pressures. Dramatic improvements in the wear properties of polystyrene are observed. While the reduction of wear rate ( $K$ ) from 3,000 to 37 with the introduction of 2 percent dimethylsilicone is significant. The extreme improvement is actually a result of improving the PV limit for polystyrene.

Because of the enhanced wear and frictional characteristics demonstrated with the addition of silicones to neat thermoplastic resins, the effect of silicone addition on internally lubricated thermoplastics was investigated. The superior wear properties of thermoplastics containing polytetrafluoroethylene (PTFE) internal lubricant have been well documented (5, 7); PTFE has the lowest coefficient of friction (0.04–0.06) of the solid internal lubricants such as molybdenum disulfide (0.12) and graphite (0.09), which are commonly incorporated into thermoplastics (8). PTFE has a lower static coefficient of friction than dynamic coefficient of friction insuring nonstick-slip properties. PTFE requires little shear energy to form a soft continuous film of lubricant. PTFE possesses an extremely low critical surface tension (18.5 dynes/cm) and, consequently, has high release properties.

It was found that much higher proportions of silicone could be incorporated into thermoplastics than had previously been possible. PTFE/silicone ratios equivalent to those in "extreme pressure transmission lubricants" can

be achieved (9). A comparison tabulated in Table 1 demonstrates wear and frictional properties for migratory internally lubricated compounds containing silicone and PTFE, and for those containing only PTFE. It can be seen that wear factor and friction generally are reduced by 30 to 50 percent. The addition of silicone migratory lubricants had the greatest effect on LPV at high velocities. This is to be expected, since high-speed failures are more directly related to wear. In acetal, for example, the PV limit doubled at 1,000 fpm in comparison to a straight PTFE-based material from 5,500 to 12,000. The ability of the silicone to continually replenish boundary lubrication accounts for the dramatic decrease in wear of migratory internally lubricated compounds at high speeds. PTFE maintains optimum wear characteristics under extreme pressure conditions and maintains a low coefficient of friction relatively independent of temperature up to 275 C. As the combined materials reach the wear interface together, they effect a synergistic reduction in wear rate. Thus, the fully compounded aceta. shows 80 percent less wear than neat acetal resin which is commonly regarded as a good bearing material. Limiting pressure velocity is improved 200 percent to 500 percent. The reduction of wear rate in nylon 6/6 resin is even more dramatic. Wear rate is reduced 97 percent and LPV is improved 300 percent to 600 percent.

The rate of migratory lubrication has been investigated by two methods. In the first, nylon 6/6 incorporating 2 percent dimethylsiloxane was molded into test plaques. The contact angle of a drop of water was observed. The specimen was wiped clean of silicone fluid. The contact angles of water drops were determined periodically. The results indicated that a complete regeneration of silicone film was effected within 36 hours. Results are tabulated in Table 2. In a second experiment, polyacetal copolymer containing 2 percent dimethylsiloxane was wiped clean of silicone with methylene chloride periodically. The greatest rate of silicone migration occurs initially, and then a gradual reduction is noted (see Table 3). The effect is accelerated at high temperatures. At the end of 36 days,

TABLE 1—WEAR AND FRICTIONAL PROPERTIES OF INTERNALLY LUBRICATED THERMOPLASTICS

BASE RESIN	LNP SERIES CODE	DI- METHYL- SILOX- ANE	PTFE %	TOTAL PTFE AND SILI- CONE %	WEAR FACTOR AT EQUILIBRIUM $10^{-10} \frac{\text{in}^3 \text{ min}}{\text{ft lb hr}}$	COEFFICIENT OF FRICTION		LIMITING PRESSURE VELOCITY		
						$\mu S$	$\mu D$	10 ft/min	100 ft/min	1000 ft/min
Acetal Copolymer..	K-1000	—	—	—	65	0.14	0.21	4,000	3,500	<2,500
Acetal Copolymer..	KL-4410	2	—	—	29	0.09	0.12	4,000	5,000	3,000
Acetal Copolymer..	KL-4040	—	20	—	17	0.07	0.15	10,000	12,500	5,500
Acetal Copolymer..	KL-4540	—	—	20	9	0.06	0.11	8,000	15,000	12,000
Nylon 6/6.....	R-1000	—	—	—	200	0.20	0.28	3,000	2,500	>2,500
Nylon 6/6.....	RL-4410	2	—	—	40	0.09	0.09	3,000	6,000	9,000
Nylon 6/6.....	RL-4040	—	20	—	12	0.10	0.18	14,000	27,500	8,000
Nylon 6/6.....	RL-4540	—	—	20	6	0.06	0.08	14,000	30,000	12,000
Polystyrene.....	C-1000	—	—	—	3,000*	0.28	0.32	750	1,500	—
Polystyrene.....	CL-4410	2	—	—	37	0.06	0.08	4,000	9,000	—

\* Exceeded PV Limit.

when samples appeared to be reaching equilibrium migration rates, the room-temperature specimen was retested for wear properties. Results were identical to those reported in Table 1. The high-temperature specimen was not tested due to the degradation observed in the acetal.

In order to determine the range of applicability of

silicone migratory lubrication, a glass-reinforced nylon 6/10 and polycarbonate resin containing PTFE were evaluated. The polycarbonate resin was found to delaminate severely if any dimethylsiloxane polymer was introduced. When a phenyl siloxane polymer was substituted for the dimethylsiloxane polymer, no delamination was

TABLE 2—CONTACT ANGLE OF WATER ON NYLON 6/6 BEFORE AND AFTER METHANOL WIPE

	INITIAL	AFTER METHANOL WIPE					
		0 Hrs	8 Hrs	16 Hrs	24 Hrs	36 Hrs	48 Hrs
Nylon 6/6 w/2 percent Dimethylsiloxane.....	87°	71°	81°	84°	86°	87°	87°

TABLE 3—CUMULATIVE WEIGHT LOSS OF POLYACETAL CONTAINING 2% POLYDIMETHYLSILOXANE

	TEMPERATURE	
	23 C	115 C
3 Days.....	0.008%	0.25%
6 Days.....	0.020%	0.27%
10 Days.....	0.030%	0.32%
36 Days.....	0.035%	0.33%

observed. This may be attributed either to the greater compatibility of the silicone due to the introduction of aromatic groups or its greater high-temperature stability (see Table 4). Table 5 compares the mechanical properties of compounds possibly containing silicone migratory lubricants to control compositions. In general, properties were maintained, although in some instances a marginal reduction was observed. This is true even in the case of glass-fiber-reinforced nylon 6/10 where the silicone might be anticipated to behave as a debonding agent.

TABLE 4—WEAR AND FRICTIONAL PROPERTIES OF INTERNALLY LUBRICATED NYLON 6/10 AND POLYCARBONATE COMPOSITES

BASE RESIN	LNP SERIES CODE	GLASS FIBERS %	PTFE %	TOTAL PTFE AND SILICONE %	WEAR FACTOR AT EQUILIBRIUM $10^{-10} \frac{\text{in}^3 \text{ min}}{\text{ft lb hr}}$	COEFFICIENT OF FRICTION		LIMITING PRESSURE VELOCITY		
						$\mu S$	$\mu D$	10 ft/min	100 ft/min	1000 ft/min
Nylon 6/10.....	QFL-4036	30	15	—	15	0.23	0.18	20,000	15,000	12,000
Nylon 6/10.....	QFL-4536	30	—	15	8	0.17	0.31	20,000	15,000	12,000
Polycarbonate....	D-1000	—	—	—	2,500	0.31	0.38	750	500	—
Polycarbonate....	DL-4030	—	15	—	75	0.09	0.15	15,000	20,000	10,500
Polycarbonate....	DL-4530	—	—	15	40	0.08	0.09	15,000	22,500	17,000

TABLE 5—PHYSICAL PROPERTIES OF INTERNALLY LUBRICATED THERMOPLASTICS

BASE RESIN	LNP* SERIES CODE	MOLD SHRINK-AGE	SPECIFIC GRAVITY	WATER ABSORP-TION %	TENSILE STRENGTH ULTIMATE	TENSILE ELONGA-TION ULTIMATE	FLEXURAL STRENGTH	FLEXURAL MODULUS	IMPACT STRENGTH NOTCHED	IMPACT STRENGTH UN-NOTCHED
Acetal.....	KL-4040	0.017	1.55	0.15	5,900	23.0	8.0	290	0.7	10.2
Acetal.....	KL-4540	0.017	1.52	0.16	5,500	37.0	7.7	250	0.9	9.1
Nylon 6/6.....	RL-4040	0.014	1.26	1.40	8,900	9.0	13.7	375	0.6	7.7
Nylon 6/6.....	RL-4540	0.014	1.18	0.80	9,600	5.5	13.6	360	0.7	7.6
Nylon 6/10.....	QFL-4036	0.003	1.45	0.15	20,000	4.0	29.0	1,150	2.2	17.0
Nylon 6/10.....	QFL-4536	0.003	1.40	0.10	18,200	5.0	27.5	1,000	2.2	16.0

\*Exact compositions may be obtained from code designations in Tables 1 and 4.

## SUMMARY

Silicone fluids may be introduced into a variety of polymer matrices provided the materials are compatible enough to form partial alloys. Aromatic backbone polymers appear to be more compatible with phenyl silicone fluids than dimethylsilicone fluids. The successful polymer blend results in materials with dramatic reductions in wear and coefficient of friction. Similar results are effected in composites of these alloys. In the glass-fiber-reinforced nylon 6/10 alloy, only a marginal reduction in physical strength was observed over the neat composite. Silicone alloys of PTFE-containing composites resulted in further reduction in wear when compared to composites containing PTFE alone. These results suggest consideration of the materials for a variety of high-speed gear, bearing and slide applications.

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