

Polymer Tribology

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In the 50th anniversary year of the Jost Report which defined 'tribology' it is appropriate to consider polymer tribology. Great attention has been given to studying metal/metal and metal/ceramic contact tribology; less attention has been given to metal/polymer and polymer/polymer contacts. Polymer components are increasingly replacing metals in structures, housings, flexures and bearings, particularly in automotive weight reduction applications. They are readily formed, by injection moulding, casting or machining with minimal waste, to give components which are lighter, cheaper, corrosion-resistant, quieter and do not require maintenance.

Polymer tribology, as their friction and wear mechanisms, is more complex than for metal and less well understood. Whereas there are well-established 'Laws of Friction' for the tribology of metal and ceramic contacts in relative motion, polymer/metal contacts generally do not follow these Laws. The reasons for this are several, including the relative softness of polymers compared to metals, their much lower thermal conductivities associated with heat generation in contacts and also significantly lower melting points. If these issues are not appreciated then polymer applications of rolling, sliding or bearing components will be 'problematic'.

The Variety of Polymers: A confusing issue is the number of polymers and their available formulations. Whereas over 300 individual polymers are characterized in the 'Handbook of Chemistry and Physics', 96th Edn., in that their physical properties and T_g (glass transition temperatures) have been determined, a useful working distinction between 'Synthesised' and 'Commercial' polymers is based on:

- are a polymer's individual physical properties suitable for applications?,
- is this polymer uniquely useful against the properties of another?,
- the cost of raw materials and production,
- the ease of initially producing the polymer and subsequent forming it into a product,

which reduces the number of commercially significant polymers to around 30.

In addition, individual polymers can be produced with a range of molecular weights or with distinctive spatial structures which affect their physical properties, particularly for polyethylene and polypropylene. Further, to improve performance polymers are offered with various additives such as glass or carbon fibre at various treat rates to enhance physical properties, mainly for physical strengths and moduli. Furthermore, polymers can be offered as either physical mixtures of different polymers or chemically combined as co-polymers. The range of available polymers is therefore immense, suitable for varied operating conditions of strength, operating temperature range, resistance to environmental degradation, friction coefficients and wear rates. Necessarily, this article is confined to the plain polymers!

The Polymer Pyramid: Polymers can be arranged on the basis of their physical properties, operating temperature ranges and cost, the 'Polymer Pyramid', Figure 1.

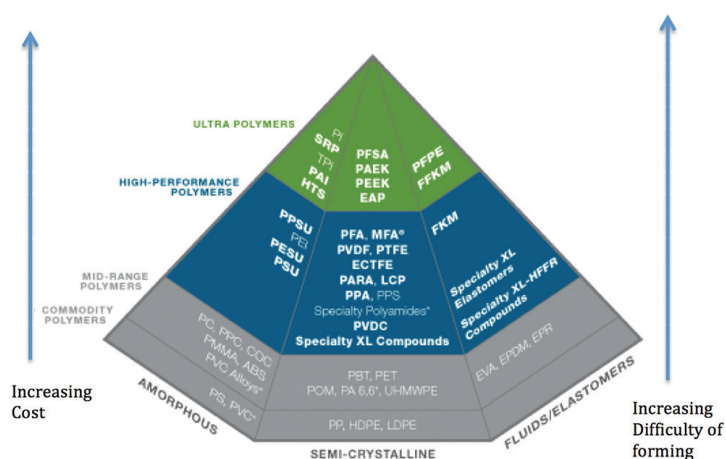


Figure 1. The 'Polymer Pyramid'

The commodity polymers of PS (polystyrene), PVC (polyvinyl chloride), PP (polypropylene), and PE (the various forms of polyethylene) are relatively weak materials with Tensile Strengths, T_s , of the order of 20MPa. They are high volume (Mt/ya), with limited temperature operating ranges up to 100°C and cheap, (<£1/kg), materials which are produced internationally.

The 'Mid-Range' polymers, often termed 'engineering polymers', such as typically PA (polyamides, 'Nylon') and PET/PBT (polyesters) have higher strengths of the order of 75MPa with continuous operating temperatures up to 110/120°C and a cost range up to £10/kg.

The 'High Performance' polymers tend to be produced in developed countries and have a higher level of physical properties, higher melting points and very good resistance to degradation and cost up to £100/kg. These merge into the 'Ultra Polymers', with very high melting points, higher strength such as the polyaramids (Kevlar/Nomex) and the PAEK family which includes PolyEtherEtherKetone, or 'PEEK', with T_g up to 100MPa, melting point around 343°C and a usable temperature range to 250°C, produced by specialist companies with prices beginning in the region of £100/kg and upwards.

Polymers and the Laws of Friction: Polymer tribology differs from metal/ceramic tribology because polymer/metal or polymer/polymer contact is predominantly elastic. The Plasticity Index of Greenwood and Williamson predicts the onset of plastic flow as:

$$\psi = (E/H) (\sigma^*/r)^{1/2}$$

where E is Young's Modulus (the major contributor), H-hardness, σ^* - the standard deviation of asperity heights and r is the assumed spherical surface radii. E/H for metals is of the order of 100, for polymers it is of the order of 10. Friction coefficients for un-additivised polymer against polymers, metals or ceramic pairs are 0.1–0.6, with a lower bound of 0.10 for PTFE.

But more importantly, polymer tribology does not follow the Laws of Friction, because friction coefficients, μ 's, vary according to:

- **normal load** - should be independent but μ 's often decrease with increasing load, up to a limit determined by deformation and contact temperature limits,
- **sliding speed**, should be independent but μ 's often decrease with increased relative velocity, limited by heat generation and increased contact temperatures,
- **temperature**, as polymers have much lower melting points than metal, related to the normal load and sliding speed used,
- **the effect of T_g** , the 2nd order phase transition, on friction coefficients due to the semi-crystalline to amorphous phase transition of a polymer is often not considered for friction/wear/temperature performance, particularly for surface layers. It is a fundamental property of each polymer, e.g., +63°C for nylon-6, +143°C for PEEK, and -1°C for PP. Friction coefficients above and below the T_g value for a polymer are usually different, reflecting the changed nature of the polymer mass at the surface. The contributions of the T_g transition to friction and wear performance of a polymer, particularly for surface layers, is not often considered in the literature.

The PV Envelope: The PV envelope, is the locus of the product of normal load (P) x sliding speed (V). It is an essential tool which defines a reliable working region for a polymer application. The test method, humidity and sample % crystallinity are further 2nd order effects on friction coefficient values. **Figure 2** shows the PV envelope for two different polymers, emphasizing that each individual envelope can be different. It is essential that the PV envelope of a polymer specified for a proposed component design is known to avoid its premature failure in service.

Static and Dynamic Friction Coefficients: The **static friction coefficient** applies to the initial effort required to start moving a body on a surface, μ_s , described later. The more commonly experienced friction coefficient is the **dynamic friction coefficient**, μ_d , which applies to the established motion of a body on that surface. The static friction coefficient of two material surfaces in contact is always higher than the dynamic friction coefficient. Contrary reports have been few, far-between and not sustained.

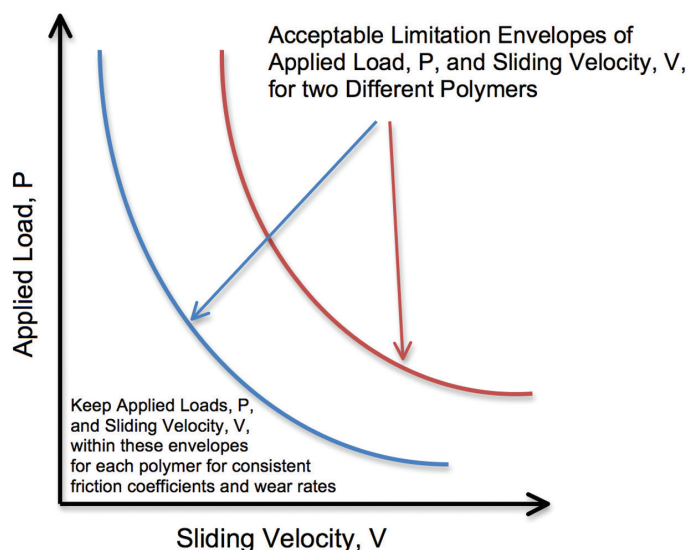


Figure 2. PV diagram plots for two different polymers

- **Dynamic Friction Coefficients of Polymers:** For objective comparison between the friction coefficients of polymers, the test conditions and apparatus must be specified. Different test methods can give different friction coefficients for the same polymer, the dynamic friction coefficients in **Table 1** used the ASTM D3702 method and apparatus at a load of 2.77kg/cm² and 253mm/s.

PTFE	0.10	PVC	0.30
UHMWPE	0.12	HDPE	0.28
antistatic	0.12	LDPE	0.60
oil-filled	0.13	Polypropylene homo-pol	0.26
Nylon 6 Cast	0.26	Nylon 66	0.25
Nylon 6 Cast, oil-filled	0.14	Nylon 66 'Super Tough'	0.28
		Nylon 66, Extrd'd.	0.26
Acetal, homo-polymer	0.20	Acetal, co-polymer	0.18
PEEK, unfilled	0.18	PEEK 30%GR	0.30
PEEK 30% GF	0.31	PEEK, 30% carbon-filled	0.22
Polysulphone	0.37	PPO/PS	0.39

Table 1. Dynamic Friction Coefficients for Some Common Groups of Polymers

The effects of polymer structure and fillers on friction coefficients are separated out in **Table 2** which shows that solid fillers usually increase the coefficient of friction. However, wear rates depend upon the particle size and hardness and thus the overall nature of the filler. Both friction coefficients and wear rates for a filled polymer need to be determined under real operating conditions of load and velocity because in some cases they can be opposite, e.g., for PEEK:

- μ for unfilled PEEK, $\mu=0.18$,
- but PEEK + 30% carbon fibre, $\mu=0.22$ but with a *decreased* wear rate,
- whereas PEEK + 30% glass fibre, $\mu=0.30$, but an increased wear rate.

Effect of Polymer Structure	
Polyolefins -	μ
UHMWPE	0.12
" , antistatic	0.12
" , oil-filled	0.13
PP, homo-pol	0.26
HDPE	0.28
LDPE	0.60
POM/Acetal -	
Acetal, co-polymer	0.18
Acetal, homo-polymer	0.20
Effect of Halogen Elements – Fluoro- & Chloro-Polymers	
PTFE	0.10
PVDF	0.24
PVC	0.30
Effect of Filler -	
PEEK, unfilled,	0.18
PEEK, 30% carbonfilled	0.22
PEEK, 30% GR	0.30
Effects of Structure and Filler -	
Nylon 6-Cast, wax-filled,	
low friction,	0.04
Nylon 6-Cast, antistatic,	
low friction	0.05
Nylon, wax-filled,	0.08
Nylon 6-Cast, oil-filled,	0.14
Nylon 6-Cast, unfilled,	0.26
Nylon 66, 30% GF	0.31

*GF is glass filled

Table 2. Effects of Polymer Structure and Fillers on Friction Coefficients

Reducing Polymer Friction Coefficients: If friction coefficients can be varied upwards, then they should also be capable of being reduced. The main techniques of reducing polymer friction are:

- inclusion of solid (soft) fillers,
- external lubrication,
- intrinsic (internal) lubrication

The **inclusion of solid soft fillers** into a harder polymer reduces friction coefficients by using the harder polymer as a matrix and the softer filler/polymer as a lubricant, forming a transfer film at the interface between the filled polymer and a steel surface. PEEK/PTFE sintered composites are a good example, the ratio of Young's Moduli, E_{PEEK}/E_{PTFE} being 8:1, giving a friction coefficient of 0.14, greater than μ for PTFE of 0.10 but less than μ for PEEK at 0.18, where in this case:

- PTFE is the soft lubricant in a harder PEEK support matrix,
- the sintered composites supports higher applied loads than is possible than for PTFE alone,
- there is clear SEM/EDX evidence of a PTFE transfer film onto the steel counterface. But the transfer film tends to be oriented in the direction of relative movement with higher friction coefficients normal to the direction of original movement.

External lubrication of polymer components reduces friction between the polymer and metal surfaces. As most polymers and their physical properties are unaffected by hydrocarbon and synthetic lubricants over a wide range of high temperatures, externally lubricated polymer components are used in many demanding applications. **Figure 3** shows a chain element for a thin packaging film stretching machine, for which there are two chains running in parallel, each 1km long, through a 165°C furnace at 8m/s. The black plastic slides in each chain element are injection moulded PEK 30, PEK is the simplest PAEK polymer family member, with 30% carbon rod content. The complete chains run on their side in separate baths of synthetic ester lubricant to achieve a friction coefficient of 0.09.



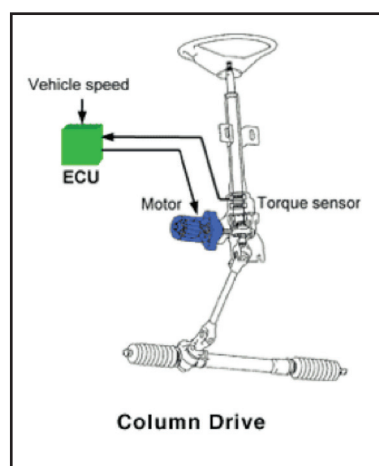
Figure 3. PEK 30 in Chain Element of Film Stretching Machine

External grease lubrication of a polymer/steel interface is used in Electric Power Steering (EPS) systems. EPS has displaced hydraulic assist steering systems in the small and medium passenger car market because of its smaller package size and weight, high reliability, low noise/ vibration and low level of 'harshness' feel to the driver. EPS systems are a low parasitic energy replacement for hydraulic power steering systems, which together with reduced weight, has rapidly penetrated the market.

One main design of EPS systems is the Column Drive system where the electric actuator is close to the steering wheel within the cabin of the vehicle, **Figure 4a**, set out diagrammatically in **Figure 4b**.

Figure 4a. EPS Column Drive

Figure 4b. Diagram of EPS Column Drive



The EPS gearbox, **Figure 5**, has a composite steel hub/nylon gear on the steering column driven by a worm gear, seen at the bottom of the housing shown in **Figure 5**. The worm gear is driven by a motor instructed by the Electronic Control Unit (ECU) from directional and magnitude signals generated by the steering wheel, as shown diagrammatically in **Figure 4b**.



Figure 5. Internal View of EPS GearBox

Figure 5 shows the internal view of an EPS GearBox, Looking down the Axis of the Steering Column. The Steel Hub/Nylon Tyre Composite Gear has a peripheral yellow layer of grease, (the steel worm is seen at the bottom of the gear).

The nylon polymer gear/steel worm interface in the EPS gearbox is lubricated by grease, the nature of which determines the friction coefficient, **Figure 6**. The baseline for consideration is the un-lubricated nylon polymer/steel interface with a friction coefficient of 0.32. Synthetic lubricant-based greases 1 and 2 reduce that friction coefficient to between 0.065 – 0.075. The use of fluorinated greases to lubricate polymers is complicated – one fluorinated grease increases the nylon polymer/steel friction coefficient to 0.15 whereas another fluorinated grease formulation, fluoro-2, reduces the friction coefficient down to 0.04.

A further point is that the fluoro-2 grease formulation has a smooth plot in contrast to the other friction-time plots, a significant consideration for the reduction of Noise-Vibration-Harshness (NVH) in the EPS gearbox. It is essential to test several types of grease to find the optimum formulation for lubricating polymers.

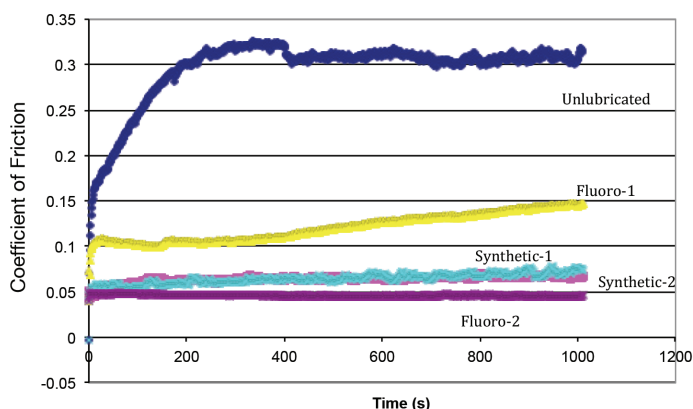


Figure 6. Friction Coefficients for Nylon/Steel Interface, Unlubricated, and Lubricated by Synthetics and Fluorinated Greases

Internal, or intrinsic, lubrication to reduce polymer friction uses, ideally, a polymer material with a low friction coefficient without external lubrication to which lubricants are added at the injection moulding, extrusion or casting stage. The melting point of the polymer limits the choice of the oil lubricant. Solid lubricants such as molybdenum disulphide, MoS_2 , and small amounts of PTFE are used. Solid and liquid lubricants are added at the injection/extrusion or casting stages of final polymer production.

For cast polymer nylons, the lubricant is added at the molten monomer stage before polymerisation. Efficient mixing disperses the lubricant as a uniform distribution within the liquid monomer which is captured and maintained by subsequent polymerisation. Liquid lubricants are dispersed as uniform microcapsules within the polymer mass. In use, wear and applied force within the polymer/metal contact will break a microcapsule of lubricant which lubricates that contact.

The reduction in friction coefficient for intrinsically lubricated nylons is dramatic, from 0.35/0.32/0.26 (according to measurement method) for plain, 'dry', nylon-6, to 0.14/0.16 for oil-filled cast nylon-6, to 0.08 for wax-filled cast nylon-6. Wax-filled nylon polymer slide/wear pads are used in the extending concentric masts of construction vehicles and cranes, **Figure 7**.

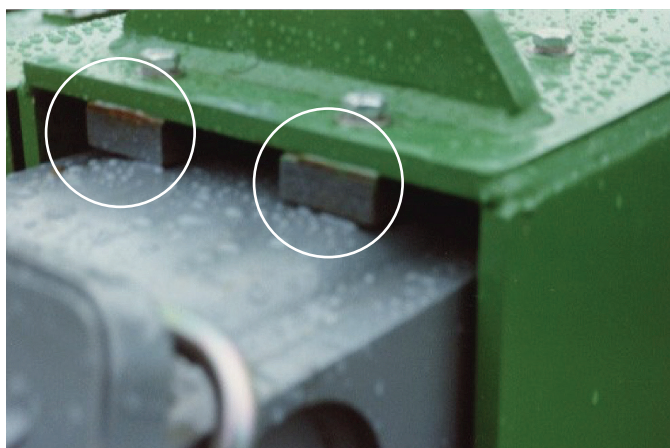


Figure 7. Wax-Filled Nylon Polymer Slide Pads, as Circled, used in the Concentric Extending Mast of a Construction Vehicle

Further reductions in nylon-6 friction coefficients are achieved by using a 'nano-fluor' oil, $\mu = 0.05$ and using a PerFluoroPolyEther (PFPE) to further reduce the nylon-6 friction coefficient, $\mu = 0.04$. The reductions in friction coefficient are increasingly costly as the required lubricants are expensive, even at low treat rates. Cost benefit analysis shows that the very low friction coefficient, intrinsically lubricated, nylon polymers are only viable for very demanding applications.

PerFluoroPolyEther Polymers – PFPE polymers have outstanding low friction performance. They are part of a large group of compounds which vary by structure and molecular weight range and can be liquids, waxes or thickened as greases. They are used extensively in fabric protection, particularly in outdoor clothing weather protection. PFPE's can be extraordinarily expensive – but only a thin film is required for effective lubrication and, as their vapour pressure is very low, that film remains.

A very useful application of PFPE lubrication is between the upholstery squabs of passenger vehicles. The micro-relative, fretting, motion of the leather or polymer upholstery as the vehicle moves gives a 'stick-slip' action which emits noise as a squeak. Whilst unlikely to degrade the contacting surfaces, the noise is annoying, particularly for the purchasers of 'up-market' vehicles. A thin film of PFPE light wax applied between the contacting surfaces of the upholstery drastically reduces the 'stick/slip' effect to the point of eliminating the squeaking effect.

Static Friction Coefficients and Stick/Slip: as defined previously, the *static friction coefficient* applies to the initial effort required to start moving a body on a surface, μ_s , and is always greater than the dynamic coefficient. The effect is known as 'stick/slip' and is universally important, from micromachining

through to the slow amplitude motions of tethered large masses such as ships. The characteristics of 'stick/slip' are that the static friction coefficient, μ_s , also increases with decrease in relative surface velocity, particularly at very low relative velocities. The dynamic friction coefficient, μ_d , also increases with decrease in relative surface velocity but is always less than μ_s . The difference between the two friction coefficients decreases with increase in surface velocity until they merge. The 'stick/slip' effect is always present; it cannot be eliminated but can be substantially reduced by using a PFPE oil or grease as a lubricant or as a component in a lubricant formulation.

'Stick/slip' affects the accuracy of micro-machining through to the safety critical mooring control of vessels such as LNG and crude oil tankers. For the latter, the 'stick/slip' motion of a vessel's mooring ropes or tow ropes can lead to unpredictable and premature failure. The iron/steel surfaces through which the ropes pass, 'the fairleads', are often of poor quality with rust scale and old, scabrous, paint, accelerating degradation of a synthetic fibre rope, **Figure 8**. 'Stick/slip' of the ropes occurs as the moored vessel rolls and the mooring ropes are alternately tensioned and relaxed.



Figure 8. Steel Vessel Fairlead with Rusty and Worn Paint Surface

A solution is to provide a smooth, non-corroding surface such as a nylon polymer insert into the fairlead, **Figure 9**, which drastically reduces 'stick/slip' and extends the life of the ropes.

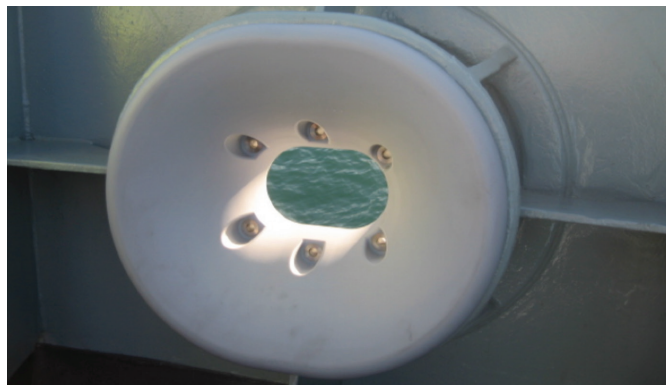


Figure 9. An Intrinsically Lubricated Nylon Polymer Fairlead Insert on a Vessel

The test rig for the nylon polymer vessel fairlead material is large, **Figures 10 and 11**. The PET mooring rope is periodically tensioned over a nylon polymer section by a hydraulic arm, first without PFPE lubrication. A 'Block' of tension events is applied through the hydraulic actuator, varying up to 150kN, a series of major and minor tension, computer controlled, events for 60 minutes. The rope will move over the central fixed sheave steadily, or not. The block of tension events causes extreme 'stick/slip' behavior to occur, **Figure 11**, with very loud, sudden, noise associated with each slip, i.e., a very loud 'bang', with the rope pattern impressed into the nylon polymer surface. The PET rope/nylon polymer surface 'dry' friction coefficient is 0.36.

A lubricated nylon sheave section allows the PET rope to flow smoothly over the fairlead sample with no 'stick/slip' and no associated noise. There is a considerably reduced wear scar, **Figure 12**, with a friction coefficient of 0.09.

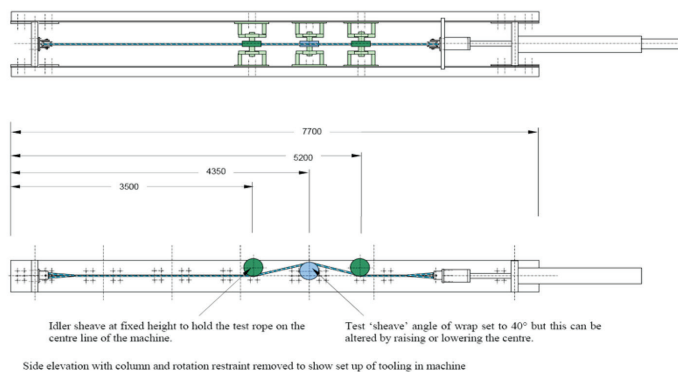


Figure 10. Plan of Mooring Rope 'Stick-Slip' Test Rig

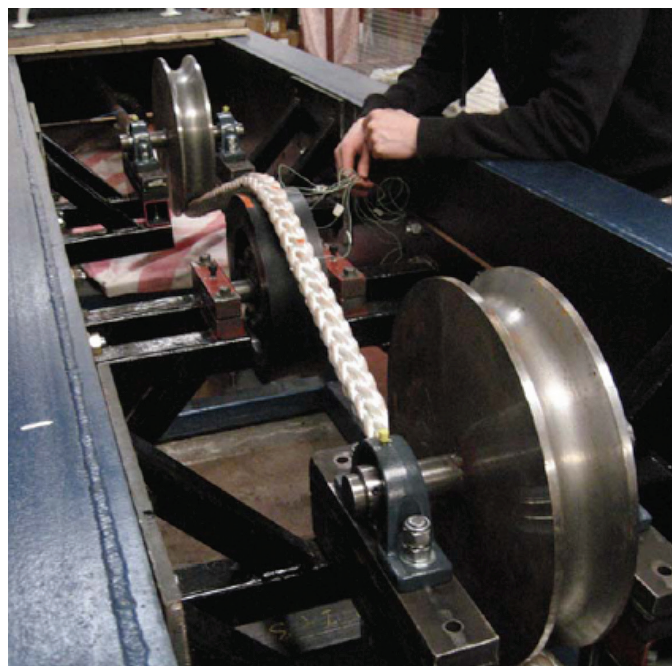


Figure 11. PET Mooring Rope Stretched over Nylon Polymer Sample



Figure 12. Effect of Extreme 'Stick/Slip' between PET Rope and Unlubricated Nylon Polymer Fairlead Section, 'Loud Bangs' with Each Slip. The Pattern of the PET Rope is Impressed into Sheave, 'Dry' Friction Coefficient of 0.36

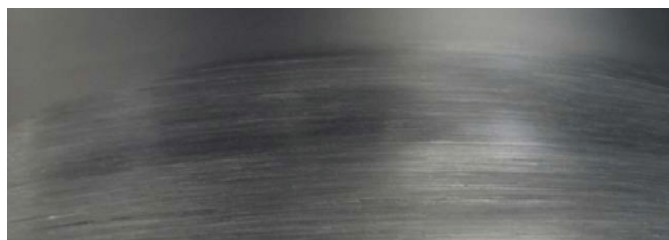


Figure 13. Very Little Stick/Slip, Low Level of Noise. Rope flows Smoothly over Sheave. Considerably Reduced Wear Scar with Lubricated Nylon Polymer Sheave, Friction Coefficient of 0.09

The Future for Polymer Tribology: There is a need for more effective lubricant additives for polymers, the criteria being:

- the additives must withstand initial chemical attack from the catalyst in casting methods, must also withstand high shear and high temperatures in injection moulding or extrusion,
- the lubricant additives must have a long operating life, low volatility and a high resistance to oxidation/degradation,
- the lubricant additives must be compatible with human contact, food contact, according to applications.

Conclusion: The tribology of polymer/metal and polymer/polymer contacts is more complex than metal/metal or metal/ceramic tribology because of the relative softness of polymers compared to metals. Polymer tribology does not follow the established Laws of Friction and a PV function locus should be determined for each new polymer application. Design conditions must stay within each polymers PV Envelope.

Friction coefficients and wear can be reduced for polymers by using internal fillers, external or intrinsic lubrication. Internal fillers must be softer than the polymer matrix. External lubrication can reduce friction coefficients, down to 0.045, dependent on the lubricant. Internal lubricants reduce friction coefficients to < 0.10, with specialised fluids down to 0.04. 'Stick/Slip' can be addressed using specialised intrinsic and external lubricants.

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