SLPMC - SELF LUBRICATING POLYMER MATRIX COMPOSITES

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ABSTRACT

The paper is surveying the current state of knowledge and results of the ESA-project "SLPMC" on a polymer composite based on PTFE. The two targets of this project are to investigate lubrication mechanisms in PTFE-based composites under tribological conditions relevant to space applications (air, nitrogen, vacuum). Secondly, to develop a new composite to fulfil future needs by space applications. Hence, in the frame of this project several new composites based on PTFE and hard fillers were defined, procured and tested on material level. Results are compared to reference materials being currently use.
This paper focuses on tribological results derived by pin-on-disc tests. (Later on testing on ball bearing and plain bearing are foreseen.) The influences of parameters like load, speed, atmosphere and temperature are discussed and compared to other already known materials.

1. INTRODUCTION

The item "Self Lubricating Polymer Matrix Composite (SLPMCC)" shall refer to a (composite) material consisting of a polymeric matrix (PTFE) and inclusions of two kinds: at first, hard fillers like short fibres made of glass or minerals, oxide particles and carbon nano fibres (CNF). Secondly, solid lubricating particles (MoS_2) are added to the selected hard fillers. For space mechanisms, such SLPMC materials exist already, examples based on PTFE are Duroid and PGM. However, Duroid 5813 production has been ceased many years ago and PGM has been selected for replacing.
In space mechanisms, lubrication by use of solids has certain advantages compared to liquid lubrication. Basically, the solid lubricant can be provided as a coating on the tribological surface or inside a composite material. For ball bearings, often a combination is used: to start immediately with good lubrication a coating is applied to the races. Secondly, in order to enhance life time, a cage is made of a composite containing similar lubricant. This lubricant is then transferred via the balls onto the race of the bearing, thereby enlarging the life times. In space mechanisms, such composites based on polymers are well known, as e.g Duroid 5813, PGM-HT (both based on PTFE), but also like Vespel-SP3 and Sintimid=Tecasint (based on polyimide). Such polymers filled with solid lubricants shall be named as "Self-Lubricating Polymer Matrix composites (SLPMC)". In space mechanisms excellent tribological properties of moving surfaces in contact constitute a prerequisite for successful operation in orbit. Moreover, life time lubrication is required, i.e. maintenance (re-lubrication) is not usual. If solid lubrication is selected, the use of composite materials comes into interest. For example, roller bearing cages were often made from Duroid 5813. However, manufacture of Duroid has been ceased some years ago. Previous material evaluation has concluded that PGM-HT is a good candidate to replace Duroid 5813.
In the last years, some questions on the PGM-HT performance were raised. This project aims at investigating on one hand the tribological mechanisms acting in such composites based on PTFE, but also general material properties like the homogeneity of the material, mechanical data, thermal expansion.

2. ENVIRONMENTAL REQUIREMENTS

2.1 Friction and (solid) lubrication under vacuum

Frictional behaviour under space (vacuum) differs strongly from terrestrial environment. Lubrication by oils and greases exhibits higher risk, since they may evaporate and re-deposit on other critical surface areas, like optical components, solar arrays and shall preferably only be used under normal conditions of temperature (-40°C to 100°C). In order to minimise these risks solid lubrication is recommended, under the assumption that it is compliant with the application (e.g. low loads). In the present case, these requirements are even strengthened by the occurrence of medium temperatures.
The behaviour of solid lubricants based on lamellar structure, e.g. graphite, MoS_2, WS_2 is well known. However, the lubricant performance is driven by the presence of water vapour which reduces friction of graphite, but degrades MoS_2; this latter is well known for low friction in vacuum environment in a wide temperature and load range. However, MoS_2 degradation due to humidity is inherent, but also well documented [1]. Polymers, e.g. PTFE, can also act as solid lubricants. However, viscoelastic behaviour, local heterogeneities and the temperature dependent microstructure may result in complex frictional behaviour.

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2.2 Rationale for selection of fillers

Main Objective in PTFE-composites is to optimise the wear of the PTFE itself towards lowest friction combined with appropriate wear. A certain wear is needed to enable the formation of a transfer film, which is needed for low friction (and that will also lower the wear). Using pure PTFE would lead to lowest friction but also to excessive wear, being unacceptable for space applications. A second aspect is the appearance of the transfer film. There is still an ongoing discussion on the optimum characteristics of such a transfer film.

The hard fillers are necessary to steer this wear process in terms of shape of transfer film and of its amount. Acc. to literature [2] hard fillers reduce sub-surface deformation and "crack propagation". [3] report that the shape of fillers steer the shape of the transfer film, round fillers are reported to allow a thicker transfer film accompanied by too high wear. Long fillers like glass fibres are preferred for thin transfer film. However, they may lead to scratching of the counter part. In order to overcome this risk of scratching a solid lubricant is added (MoS_2). In materials like Duroid5813 and PGM-HT glass fibres are used in combination with MoS_2. However, studies have also tackled other mineral fillers like particles or whiskers.

Following literature and experience from space applications the following filler types were selected for the composites in this study:

- Glass / mineral fibres with varying diameter
- SiO2 particles (same chemistry, but "round")
- MoS_2 in addition to hard fillers

Their respective amounts were selected to be close to materials already in use in space applications.

2.3 Requirements for use of polymers in space

For use of materials in space, the European Cooperation for Space Standardisation (ECSS) has defined a check-list [4],[5]. However, in the framework of this ESA-Project, as different filler combinations shall be studied, only "core-properties" are investigated i.e.:

- Density and Microstructure
- Outgassing acc to ECSS-Q-70-02
- Tensile properties and hardness (ShoreD)
- Thermal expansion
- Friction and wear by Pin-ON-Disc

3 EXPERIMENTAL

3.1 Materials and manufacturing

There exists a large number of international manufacturers of PTFE-based composites. Most of the PTFE-based composites are usually produced by Free-Form-Sintering (FFS): the PTFE powder is cold pressed in a mould and afterwards free-form-sintered in an oven. The sintering-process is necessary for the composites to achieve the final strength of the semi-finished or finished parts.

Another process for the production of PTFE-based composites is called HCM, Hot Compression Moulding. This high-pressure sintering method is similar to the methods used in powder metallurgy, using a press and heatable moulding dies. The applied pressure and temperature profile has to be adapted to the material processed and to the dimension of the die, since a uniform heat penetration and compaction of the material (composite) is important. This HCM method can produce plates with dimension of for example 1000 mm x 300 mm and thickness of up to 100 mm.

The difference to the FFS process is that the part remains in the mould during the whole process. The HCM process is more complex, time- and cost-intensive and allows better mechanical properties. So this HCM method is rarely used in the manufacturing of PTFE composites. Sintimid Ensinger GmbH has the experience and the equipment for FFS and also for HCM.

About 20 years ago, it was found that PTFE composites produced with the HCM method compared to the FFS method show higher strength and lower porosity. Hence, special PTFE compounds can be produced with this HCM method.

Designation of grade	Composition Fillers in w%	Comment on fillers (size)
Pure PTFE	--	--
C01-25G-10M	25% Gf 10% MoS_2	Glass fibre ∅13µm
C02-20G-10M	20% Gf 10% MoS_2	Glass fibre ∅13µm
C03-15G-10M	15% Gf 10% MoS_2	Glass fibre ∅13µm
C09-15M-10M	15% Mf 10% MoS_2	Mineral fibre ∅3µm
C06-25S-10M	25% SiO_2 10% MoS_2	Particles ∅1µm
C07-15S-10M	15% SiO_2 10% MoS_2	Particles ∅1µm
C10-10C-10M	10% CNF	Carbon Nano Fibres ∅0,1µm
C11-03C-10M	03% CNF	Carbon Nano Fibres ∅0,1µm
Ref-P2	Gf & MoS_2	Glass fibre ∅15-25µm
Ref-F1	Gf & MoS_2	Glass fibre ∅15-25µm
Ref-duroid5813	Gf & MoS_2	Glass fibre ∅<10µm

Table 1: Compositions (C01-C10) manufactured by ENSINGER and selected for testing. Reference materials P2, F1 and Duroid (all Matrix: PTFE, composition for Ref-materials not known, fibre size derived from cross sections)

The compositions selected for the study are shown in table 1. All composites labelled "Cxx" were produced by HCM by ENSINGER SINTIMID GmbH. Reference materials were provided by suppliers from Europe (F1) and US (P2) but without detailed information on the composition. (Their general microstructure is not to far from C02/C03 including fibres and MoS_2 flakes)

The mixing of CNF to PTFE was done by AAC. HCM discs were produced by ENSINGER and samples for tensile, CTE and friction testing were (dry) machined out of semi-finished parts.

3.2 Tribological test devices and parameters

For testing of friction and wear a **High Vacuum Tribometer** based on a Pin-On-Disc configuration was used (Fig.1). Test atmosphere were air, vacuum and nitrogen; the tribometer is capable of running under Martian atmosphere (6mbar of CO_2). A heating/cooling system enables testing between -100°C and +300°C. Friction forces could be resolved by +/- 0.02N. The software enables full control of the test as well as several motion types, like unidirectional or oscillating.

Pins were machined from all materials with spherical tips of curvature 18 mm. Two loads were applied: 1N and 5N. The lower load was selected to achieve a mean Hertzian contact pressure (Pm) at beginning of the test of 2/3 of the yield strength (Ys) of the polymer [6]. From this requirement and the curvature radius of 18 mm, the calculated loads were 1-2 N for low load. To compare with references tests a load of 5N were added (Testing in [7] was done at 5,5N at radius of 18mm for PGM-HT, Duroid). Further parameters for friction tests were: oscillating motion (stroke approx. 20mm), speed 0.1 m/s, air with 50%rH, vacuum 10^{-6} mbar, nitrogen), temperatures 25 and 80°C. As counter material, a stainless high carbon and high nitrogen steel (AISI440C) was selected. Disc were grinded before friction testing to Ra~0.1µm. All samples were ultrasonically cleaned before testing.

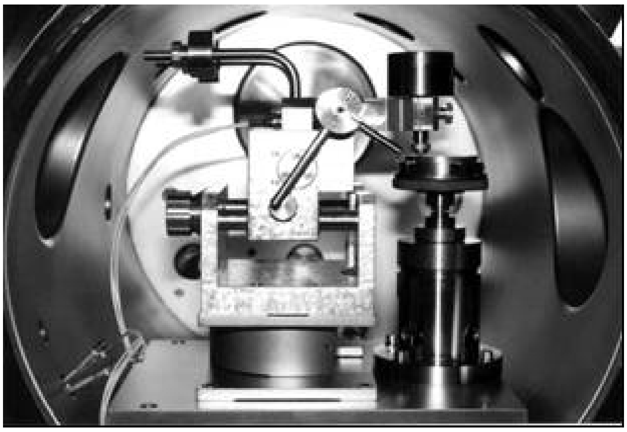

Figure 1: High Vacuum Tribometer (Inside view). Pin and disc holding, heating system not shown.

All compositions were tested with the "core parameters", a limited number was tested with "optional" parameters too (especially with low speed).

Program	Env	Load (N)	Speed (m/s)
Core:	Air	5	0.1
	Vac	5 and 1-2	0.1
	Vac-80°C	5 and 1-2	0.1
Optional:	N2	5	0.1
	Vac	5	0.01 (optional)

Table 2: Overview on test conditions (oscillating motion with ~20mm stroke)

4 RESULTS on FRICTION AND WEAR

4.1 Screening of composites

In the following images (Fig. 2 to Fig. 9), plots of the friction coefficient as function of cumulated sliding distance are shown for each tested composition. Each plot covers all tests done. Such representation allows performing an assessment of the dependence between friction and testing parameters. Hence, no details on each test are given, but just deviations are highlighted.

As overall behaviour a slight running-in with increase of friction until approx 200m sliding distance is seen. After that in most cases friction coefficient stabilises in a range of 0.2-0.3. The "steady-state" friction level is generally very similar between the environments humid air (50%rh) and vacuum.

However, for certain compositions related to low load/high speed or high load/low speed, a "super-low-friction" regime appears. The starting point for super-low friction is not fully reproducible.

The first three compositions are based on a variation of content of short fibres (C01-C03). It can be seen that for certain parameters a "super-low-friction" regime is found, which appears at unpredictable times of sliding. This is in most cases related to tests at low load and or lower speed. This effect seems to emerge with higher glass fibres content (>20%).

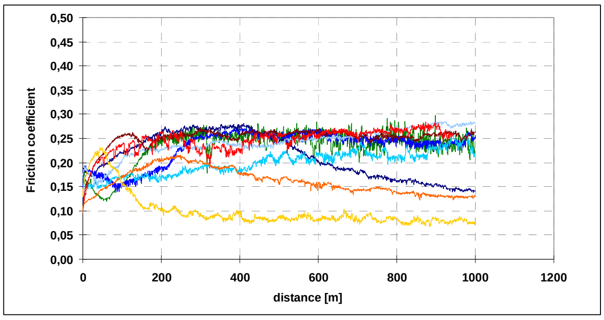

Figure 2 Composition C01 (..25GF..): Friction as function of test duration, partly super-low-friction for low load and at 80°C.

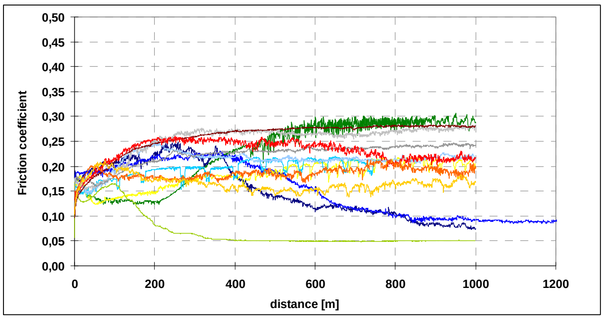

Figure 3: *Composition C02 (..20GF..): Friction as function of test duration, partly super-low-friction for low load/high speed and high load/low speed (all at RT).*

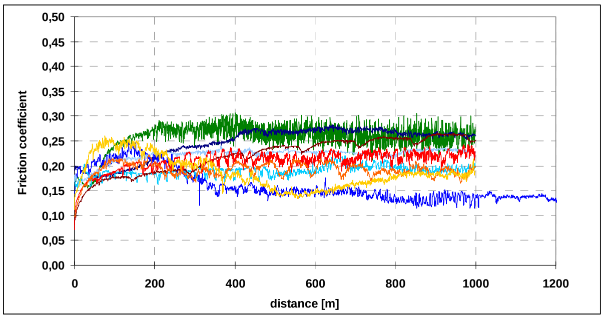

Figure 4: *Composition C03 (..15GF..): Friction as function of test duration, super-low-friction not clearly identified (low load at RT).*

Concerning its microstructure Ref-Material-P2 seems to be close to C01-C02 regarding size of hard fillers and the addition of MoS_2. Its behaviour is quite similar to C02: super-low friction emerging for low load or low speed.

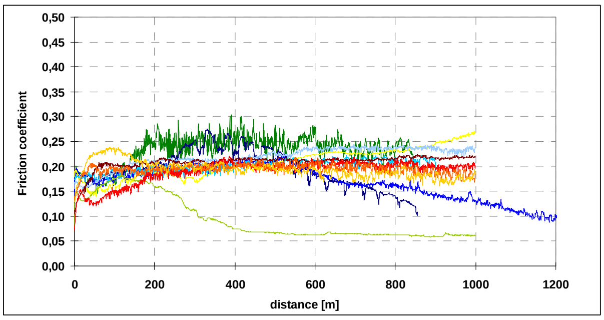

Figure 5: *Ref-Material-P2: Friction as function of test duration, partly super-low-friction for low load/high speed and high load/low speed (all at RT), similar to C02.*

In the next compositions the shape of the hard fillers were varied. Composite C06 has as hard filler SiO2-particles. Here, the super-low-friction regime is found in almost all cases: not only at low load but also at high loads, and on both temperatures (RT and 80°C).

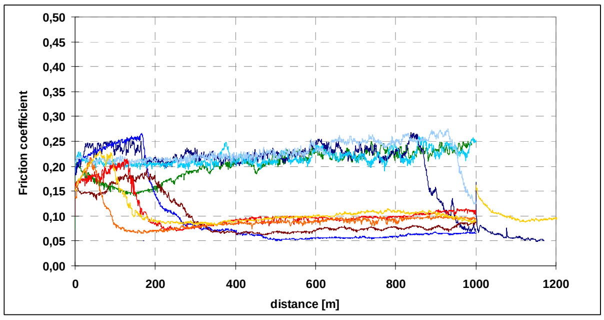

Figure 6: *Composition C06 (…25SiO2…): Friction as function of test duration, super-low-friction in almost all tests.*

In the last two composites, fibres of different size were used. C09 is filled with a mineral fibre being thinner than the glass fibres mentioned above and MoS_2. This mixture leads to constant friction being almost independent of all test parameters within 0.17-0.27. No super-low-friction regime is evidenced.

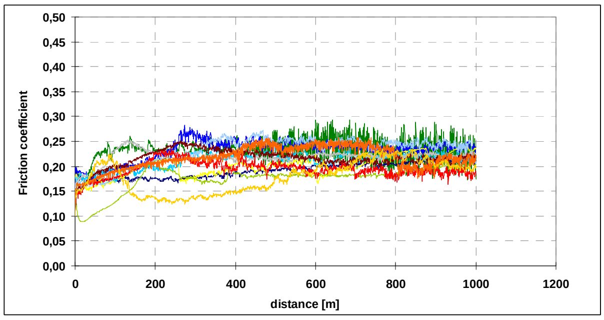

Figure 7: *Composition C09(..15MF..): thin mineral fibre and MoS_2.*

Composite C10 is filled only with carbon nano fibres (CNF) and no MoS_2. Overall behaviour is similar to above composites, increase during running-in with becoming constant with time. Average friction is slightly higher (0.25-0.33) than for the C09 but also independent from test parameters. Only in air a step is seen. (it will have to be confirmed if this is significant or statistical spread.)

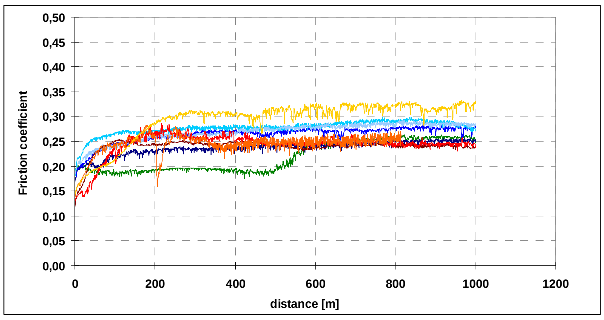

Figure 8: *Composition C10 (..10CNF..): Friction as function of test duration, using CNF without MoS_2*

Finally, a second reference materials "F1" was tested. It is also based on PTFE filled with glass fibres and MoS_2. The exact composition was not communicated by the supplier. Microstructural investigation shows the size of glass fibres being approximately similar to Reference material P2 and composites C01-C03. It shows in principal similar behaviour with super-low-friction at RT (low load). Exception is an increase of friction when testing in N2.

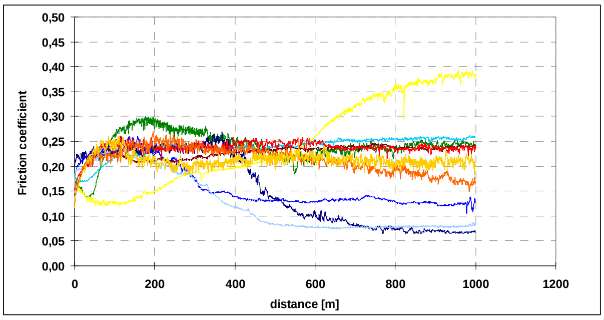

Figure 9: Ref-Material-F1: Friction as function of test duration, high friction in N2.

4.2 Mean friction

Each test was assessed defining the "steady state phase" from its end. It means in case of the super low friction regimes, the "steady state phase" represents this regime. From this whole "steady state phase" an average value and the peak value were calculated. (Figure A1 in the Annex shows all derived values.)

Again overall trends are of interest. It has to be concluded that the chosen compositions revealed almost similar mean friction being close to 0.2. The composites C09 and C10/C11 show the narrowest scattering of friction coefficients in all test conditions.

Composites with large glass fibres (C01,C02, C03, P2 and F2) combined with MoS_2 show the appearance of super-low-friction regimes. Also composites with combination of SiO_2–particles and MoS_2 (C06, C07) seem to promote this super-low friction.

Composites with smaller fibres (C09) or CNF only (C10, C11) do not show this regime.

This effect is not reported in literature [11] on Duroid or PGM-HT. However, testing in [11] was done at higher loads.

The super-low-friction regime is found preferably at low loads (1-2N) with friction coefficients in range of 0.07-0.12. It has to be said, that this super-low-friction regime was not reproducible. (This friction coefficient is close to that of pure PTFE or pure MoS_2.)

4.3 Wear factors

Wear factors were determined by measuring the diameter of the contact areas on the pins after testing. From that the lost volume of the sphere was calculated and divided by the test load and the cumulated sliding distance.

Again an overview on trends is being discussed. (please refer to figure A2 in the Annex). Generally, all compositions show reasonable low wear factors in range of 10^{-5} to 10^{-6} mm³/Nm compared to pure PTFE (>>10^{-4} mm³/Nm, would mean a values of >1000 if added to Fig. A2 in Annex).

The compositions C09, P2, F1 show overall test conditions the lowest wear factor of 5 to 10 (times 10^{-6}mm^3/Nm) with some scattering to 20. These values are around or lower than reported for Duroid in [11]. (See Fig. A2 in Annex.)

For composites C1-C3 higher wear rates are visible 5 to 25 (times 10^{-6}mm^3/Nm). The only trend can be seen for these C1-C3: when decreasing the glass fibre amount from 25 to 15m% the wear factor at high temperatures decreases.

The lowest wear factors combined with lower scattering are found for C10/C11 (based on CNFs only). Partly high wear rates can be seen in the composites with SiO_2 particles (C06/C07). This would fits to literature, when stating that round fillers are not that efficient as "long" ones.

4.4 Discussion – Wear tracks on discs

As discussed in literature the shape of wear tracks is of interest. A selection of wear tracks were investigated by optical microscopy. At first glance, during start of testing grooves on the steel discs are filled with transfer particles. In case of longer testing and/or higher loads the transferred amount increases. In general, the tracks show dark brown appearance (except for a track with pure PTFE where gross amounts of flakes are attached).

A determination of the transfer film by SEM was not possible. This means that the transfer films are too thin to be detected by SEM. The only way to "see" the tracks is by use of a so-called in-lens detector, which turns the SEM to be more sensitive to near surface features. But any EDAX analysis does not show transfer elements (like Mo/S, F).

4.5 Discussion - Influence of parameters

Contact pressure / Load: there is an influence of load on friction visible for composites with glass fibres of larger diameter (C01-C03, P2, F1). Following the current results, a low friction regime may occur after some running time. This effect is not fully reproducible at moment. It is more likely when testing at low loads (so far not done in literature, e.g. [8]). However, in some cases after longer testing times it also occurred at higher loads. The effect was also visible in particle filled composites (C06/C07), but there it was combined with definitely higher wear.

Reversible effect by load: It is worthwhile to mention that the super-low-friction appears after some time of sliding, i.e. after some wear. This leads to the assumption that this decrease of friction is related to the contact pressure falling under a certain critical value. At first glance, the important question is if this effect is reversible. Using composite C02, a test a low load (1-2N) was started. The effect occurred at ~600m sliding duration. Then the load was increased to 10N and the effect vanished immediately, i.e. friction increased to typical levels of~0.2. It is concluded that a change in loads during running may change the friction, might lead to improper control in drives.

After increase of the load, also a higher wear rate was measured. (for this test the shortening of the pin was measured on-line. The lower plot shows the shortening of the pin, the slope during the first part of the test at low load shows a lower slope than the second part at high load). This means that during high loads higher friction is seen, but also more extraction of solid lubricant.

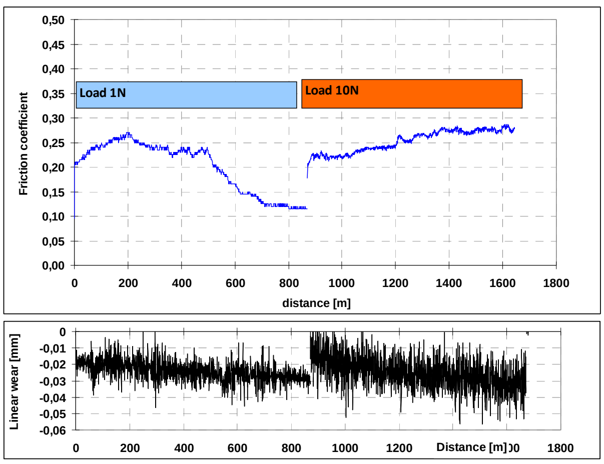

Figure 9: Composite C02 (..20GF..): Super-low-friction at low loads disappears after increase of load. Linear wear is high for higher load (steeper slope on the right)

Speed: only selected composites were tested under high load at lower speed (0.01m/s). There is again an influence between larger fibres and low speed visible: composites with glass fibres of larger diameter (C02, P2, F1) show definite super-low friction, whereas small fibres (C09) do not (within current testing distance).

Temperature (+80°C): in general, the typical friction in range of 0.2 is observed in almost all conditions and composites. Only exceptions are for C01 at low loads (25%GF) and for SiO_2 filled composites at all loads.
Looking on wear factors the lowers scattering at low values is seen for C09 and C10/C11. The only trend is visible for the C01-C03: when increasing the fibres content the wear increases (only at higher temperature not at room temperature). The average friction coefficients are lower than reported for Duroid @60° by [11] being ~0,38.

5. CONCLUSION

The first main objective of this study was to define a set of compositions considering on one hand successful materials like Duroid and materials being currently in use but also with a wider scope on fillers considering knowledge from literature and experience.

Secondly, new compositions were designed to target low friction and appropriate wear in vacuum until +80°C and to a lower extend for low friction in air.

Overviewing test results on material level so far, encouraging properties are seen for all formulations: in all cases wear rates were definitely lower than for pure PTFE. The highest wear rates were found for particle fillers (SiO_2) at RT, followed by C01 (25GF). This means that the strategy for selection of fillers was successful, underlining that fibre-like fillers are more effective.

Composite material (C02) with PTFE/ Glass fibres/ MoS_2 with 20m% glass fibres shows similar friction and wear rate than a US material (P2) and European material (F1).

Composite material (C09) with PTFE/ Mineral fibres/ MoS_2 with much smaller diameter mineral fibres (C09), compared with the glass fibres of materials like C02, shows similar friction and wear rate than Duroid5813.

All composites with larger glass fibres (C01,C02,C03,P2,F1) show a load dependent friction coefficient. This effect seems - at first glance - to be reversible.

SiO2-Particles as fillers did not show improvement compared to all fibres (even despite of MoS_2 having been added).

The composite (C09) with mineral fibres (of smaller diameter than the glass fibres) show most homogenous friction and does not show a load dependence of the friction coefficient.

Apart from standard formulations based on glass fibres, nanofibres might be an interesting option, as friction is found almost independent of environments/temperature and independent of load (~0,25-0,3 even without MoS_2).

Summarising all results, it can be concluded that on material level promising alternatives to current commercial PTFE-based materials could be identified. Moreover, two candidates may allow a new material being closer to Duroid than the commercial materials.

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ANNEX

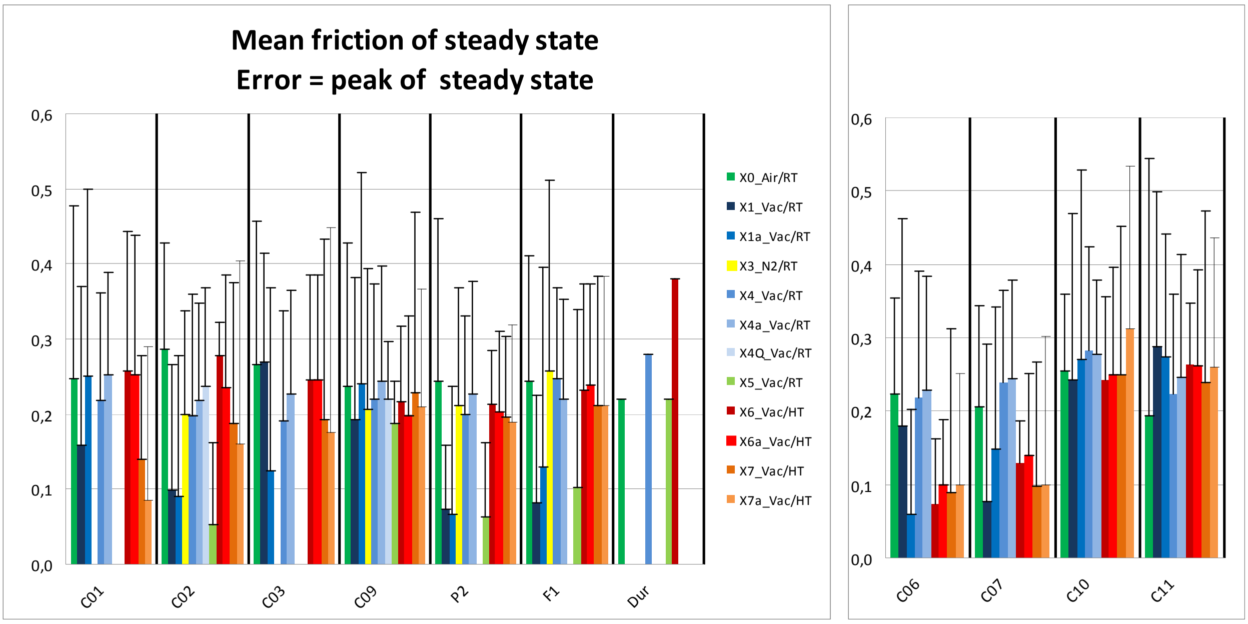

Figure A1: Pin-On-Disc tests: Mean friction coefficients derived from steady state (Error bar is peak value of steady state phase), Composites with larger glass fibres (C01,C02, C03, P2 and F1 and MoS_2 shows the appearance of super-low-friction regimes, C09 has the smallest scattering of friction coefficient. Composites with SiO_2 and MoS2 (C06,C07) are even more prone to this super-low friction. Composites with CNF only (C10,C11) show also small scattering of friction being slightly higher than for C09. (Data for Duroid ("Dur") estimated from images in [11].)

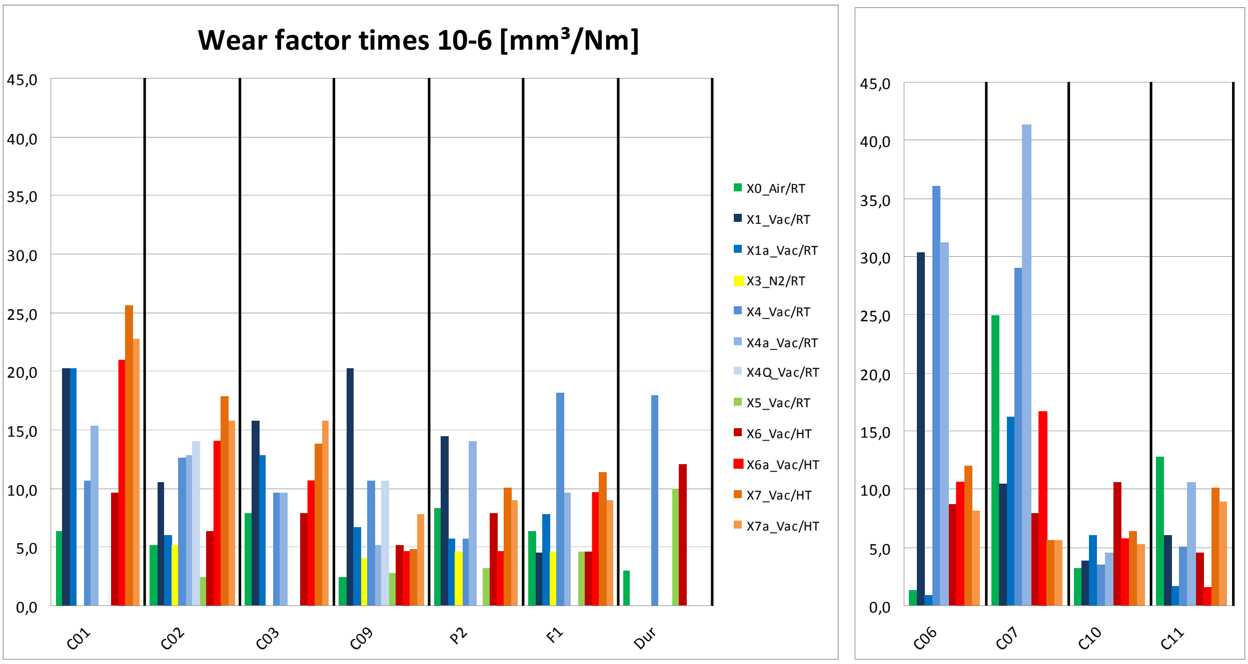

Figure A2: Pin-On-Disc tests Wear factor (calculated from wear diameter on pins after test, error of measurement about +/-1): These higher loads (5N) were also used in reference tests [11]. (Speed 0.1 m/s and 0,01m/s for series X5 only, counter material AISI440C). (Data for Duroid ("Dur") estimated from images in [11] tested against AISI52100.)