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RESEARCH OF COATINGS OF HYDRODYNAMICALLY LUBRICATED SLIDING BEARINGS FOR COMBUSTION ENGINES

RESEARCH OF COATINGS OF HYDRODYNAMICALLY LUBRICATED SLIDING BEARINGS FOR
COMBUSTION ENGINES

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Research of Coatings of Hydrodynamically Lubricated Sliding Bearings for Combustion Engines

Zadání dizertační práce:

Cílem disertační práce je studium nové formulace ložiskové vrstvy s pokročilými tribologickými vlastnostmi.

- Strukturní a tribologická charakterizace základní vrstvy PAI polymerního povlaku od Daido Metal
- Sledování možné interakce mezi mazivy a ložiskovými plochami, zejména v okrajových podmínkách
- Studium vlivu přísady $\text{Ca}(\text{OH})_2$ na tribologické chování povrchu PAI kluzné vrstvy

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ABSTRAKT

Hlavní náplní této dizertační práce je výzkum a vývoj nové povrchové vrstvy pro kluzná ložiska na bázi pevných lubrikantů v polyamid-imidové polymerní matrici se zlepšenými tribologickými vlastnostmi. Podklady pro materiálovou kompozici vzešly z expertízy komerčně dostupného povlaku, respektive jeho povrchovou analýzou v mezních operačních podmínkách. Charakterizace mazného oleje před a po tribotestování společně s detailní povrchovou analýzou dala podmínky pro vznik materiálové formulace. Další část práce se zabývá studiem přípravy a vývojem aplikačního nanášení s přípravou polymerní směsi. Nakonec je popsána studie vlivu sulfidu molybdeničitého a grafitu, jakožto pevných lubrikantů pro zlepšení třecích vlastností a hydroxidu vápenatého pro potenciální zlepšení otěruvzdornosti výsledného povrchu pro palikaci kluzných ložisek.

ABSTRACT

The aim of this thesis is the research and characterisation of new sliding bearing overlay with advanced tribological properties based on the polyamide-imide matrix and solid lubricants. The background for the material composition came from the joint initial expertise of commercial coating layer, respectively its surface observation under boundary operational conditions which provided input for improved wear and friction characteristics. Oil characterisation before and after tribotesting and detailed surface chemistry analysis was performed to investigate polymer coating behaviour in stressed lubricated conditions. Further development of coating technique with preparation of newly formulated paint is introduced. Finally, the developed PAI coating with MoS₂ and graphite as lubricants for frictional improvement and calcium hydroxide as potential wear improvement additive were studied and evaluated for bearing application.

KLÍČOVÁ SLOVA

Kluzná ložiska, povlak, mazání, tribologické vlastnosti, opotřebení, tření.

KEYWORDS

Sliding bearing, coating, lubrication, tribological properties, wear, friction.

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Declaration

I declare that the doctoral thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete.

.....
student's signature

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2 INTRODUCTION

Automotive industry tends to more environmentally friendly and more efficient combustion engines. There are several approaches how to achieve this. One of the options is engine downsizing which goes along with high power densities resulting in substantially increased local contact pressures of rolling or sliding contacts and leading to enhanced danger of seizure [1]. Highly affected machine component by this trend are engine bearings. They are designed for increased fatigue loads but also conforming the variations in alignments [2]. Further needs for tribological requirements on the bearings include low friction, higher wear resistance, embeddability, conformability as well as corrosion resistance, etc. Therefore, research needs to compromise tribological properties, mechanical strength, and chemical performance of the material [3, 4, 5, 6, 7].

Recently, to satisfy the above needs for bearing material, resin overlays, where solid lubricant is dispersed in a resin binder, are being developed [8,9,10]. Due to the beneficial effect of solid lubricants on friction, wear is less likely to progress compared with conventional Al-Sn-Si based bearing alloys. Several inorganic materials (e.g., boron nitride, graphite) can provide excellent lubrication [11] from which MoS₂ is used in the studied resin overlay. The layer (which contains CaCO₃) helps to improve seizure properties of the bearing as well as good embeddability [12].

In tribotesting where loading is systematically applied to the lubricated bearing surface, some changes in material composition can occur resulting in different tribological performances of the surfaces. The changes refer to structural changes between the sliding surfaces which have effects on the tribological conditions [13]. Formed tribolayer can protect or contribute to the degradation of materials in contact [14] as well as influencing the resulting performances in the application. Rough surfaces formed in sliding contacts increase the local stress [15]. Tribo-chemical interactions, tribo-oxidation of formed tribolayers or debris can be formed which may cause material failures [16,17].

Understanding of mechanism and kinetics of the layer's formation, stability and tribological behaviour was important for further material study and research. Oil characterisation before and after tribotesting, together with surface chemistry analysis, was performed to find out degradation products and interactions towards tribolayer formation and material structure changes of the used bearing shell. The results led to understanding of several material phenomena and gave an input for material selection and further development of the bearing surface layer.

The goal of the dissertation was to study and research new potential for sliding bearing overlay with advanced tribological properties. Since the spectrum of the goal was not entirely specific and the direction was needed, joined expertise and past research in Daido Metal, the bearing producer has been done. Therefore, exchange of knowledge in product performance and subsequent analytical approach with the help of AC2T research GmbH (Austrian Competence Center for Tribology) in Austria was carried out to achieve the material knowledge base as a core feature in further development.

Initially the proposed methodology for the comprehensive description of the composition of tribolayers was generated by the operation of bearings lubricated with engine oil and evaluation was carried out on commercially available polymer coating. Detailed topography, morphology and chemistry of new and stressed surfaces of sliding parts on engine bearings were characterized by appropriate surface analytical tools. The findings served as a

feasibility study of the usefulness of analytical tools contributing to further material research on new developed coating and put the valuable inputs for formulating the new paint for coating.

The positive tribological effect of molybdenum disulphide was already confirmed and has been studied by many as a well-known solid lubricant [18]. That is the reason why it has been chosen as solid lubricant additive also for new studied coating. It has lamellar structures consisting of a stack of hexagonal sheets (planes) with strong covalent bonds and weak Van der Waals forces between the planes holding them together [19]. This lead to an idea to use Calcium Hydroxide and its hexagonal form of sheet plates in the polymer matrix of polyamide-imide (which is used for its heat resistance). The study covered the laboratory testing of resulting coating and preliminary formulation and preparation. The application method needed to be developed together with laboratory testing for tribological characteristics.

3 TRIBOLOGY OF SLIDING COMPONENTS

Tribology is in existence since recorded history, and there are well documented examples from history how early civilizations developed bearings and low friction surfaces [20]. The scientific study of tribology has the long period as well. Many laws of friction such as proportionality between normal force and limiting friction force were generally associated to Leonardo da Vinci in the late 15th century. On the other hand this multidisciplinary study is the domain of last two centuries and most of the knowledge is being gained since the Second World War.

Tribology is a science focused on friction, wear and lubrication of interacting surfaces in relative motion. The term is derived from the Greek word 'tribos' meaning rubbing or sliding.

Wear is the main reason of losing mechanical properties of material components. Therefore any reduction in wear could result in considerable savings. Friction is on the other hand cause of wear and energy dissipation. It results in easy implication that by friction control we can achieve a considerable saving. It is estimated that one third of the world's energy resources in present use is needed to overcome friction in one form or another. Lubrication is an effective tool for controlling wear and reducing friction. Tribology is a field of science which applies an operational analysis to problems of great economic significance such as reliability, maintenance and wear of technical equipment ranging from household appliances to spacecraft [21].

4 ENGINE BEARINGS

Engine bearings are the representatives of sliding bearings. Compared to the rolling bearings, sliding ones are easier to produce and therefore cheaper. The reason why they are used in engines is primarily in their ability to withstand high loading, dirt and especially vibration. Also important is that they can be assembled much more easily compared to the rolling bearings.

The engine bearings are loaded dynamically due to piston cycles in the engine. We are therefore talking about the hydrodynamic bearings (direction and size of load varies over time).

Hydrodynamic bearings are then distinguished according to the direction of force applied to the bearing:

- Radial – loading is applied perpendicular to the axis of bearing,
- Axial – enable to transfer the load in axial direction (to the axis of bearing),
- Combined – able to combine both the force directions (e.g. conic shape bearings).

From the design point of view we distinguish between bushings (unseparated bearing) and half shell bearings which can be seen also in Figure 1. The main focus of this dissertation is towards the connecting rod bearings (rod bearings) where the higher load is applied and special material is required.

Half shell engine bearings are a vital construction part of engines which help to convert reciprocating motion of the pistons into the rotary motion of the crankshaft. The main application is in the combustion engine [22]. The loading is generated by pressure of gases

in cylinder and inertial forces of reversible and rotating unbalanced masses. These dynamic forces have the main effect on the hydrodynamic oil film generation as well as on the fatigue of resulting material. The reasons of the separation into two half shells are mainly because of easy manipulation assembly and especially maintenance. Bushings in general are not that easy to dismantle from shaft and moreover, they are not recommended be used repeatedly [23].

There are several kinds of bearings used in engine (see Figure 1).

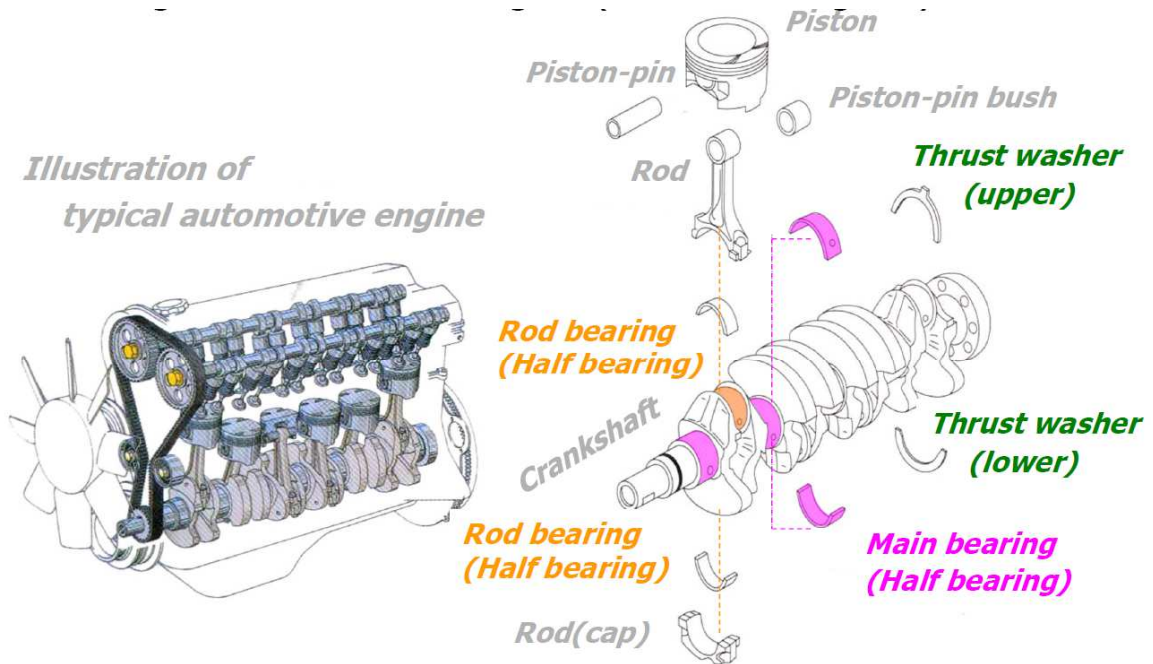


Figure 1 Illustration of typical engine bearings in automotive combustion engine part [24]

Considering the current trends of engine market, also increasing working cycles is among the targets. It results in increasing requirements on reliability and durability of sliding parts in higher rotation speeds and increased loading [25]. With increased sliding speed, maximum of hydrodynamic load bearing capacity is theoretically increased. On the other hand, it's also increasing the friction on the bearing, which generates temperature. This temperature has effect on the bearing as well as lubricant viscosity which is decreasing with increased temperature and that is what has effect on the load bearing capacity of hydrodynamic oil film. All of these phenomena result in the specific material selection on each engine bearing part separately calculated.

4.1 Materials

Bearing materials need to have special properties to operate successfully in machine parts. These materials depend on the type of bearing, type of lubricant and the environmental conditions. There is no single material satisfying all the applications [26].

There are several vital material properties for bearings. The overall need for strength and stability of the shape, the steel is considered the best material. As other unique properties like wear resistance, fatigue resistance, conformability, anti-seizure, and embeddability characteristics, etc. (described later) varies depending on the speed, size and changes in load, shaft (counterpart) materials, lubrication method and environmental factors such as

temperature and humidity. The important aspect in designing is therefore selecting proper sliding bearing material which can work in emergency conditions. It is a stage in the process where the system is running at low rotation speeds (mainly stop and start of the machine). Bearing is led into boundary lubrication regime, where thickness of oil/lubricant in the contact is low between the contacting areas, and localized contact of the counterparts (bearing and shaft) can appear and these phenomena can then lead to the seizure of bearing.

Good material therefore has to exhibit fatigue performance and compressive strength which will lead to sufficient load bearing capacity. Simultaneously, bearing has been conformable to certain surface deformation of parts which it is belonging to.

There are a lot of requirements whereas some of them are antagonistic and therefore the multi-layered material combinations have been developed in past decades. The key properties characterizing bearings are described below.

Compatibility

The operation is characterized by hydrodynamic regime when the shaft is separated from the oil by lubricant film. Starting and stopping the engine or even during the engine run, the shaft and the bearing come into the contact. The boundary or mixed lubrication regime occurs. Localized heating occurs during the contact causing some welding of parts and can lead to damage at these points. This phenomenon usually results in scoring damage to both the shaft and bearing materials. Compatibility leads to the ability of these material combinations to resist welding and scoring.

Embeddability

Engine operation causes wear of some constructing parts and forms wear debris which eventually comes into bearing clearance by the lubricant. Unfortunately, most often it is not possible to be removed by oil filter. The particles are still bigger than the minimum oil film thickness in lubricated components (e.g. crankshaft bearings). In order to operate successfully, the lubricated component must have a layer with ability to embed small hard particles into the surface without damaging the counterpart (in our case the shaft surface) as well as stopping to form scratches on its surface. The side effect due to hard particle pollutant is the increase in friction of the bearing which can eventually cause friction increase [27]. Ability of bearing surface to embed particles to the softer bearing material is essential in order to prevent possible scoring damages.

In Figure 2, the hard particle has produced an undesirable score on an aluminum/tin alloy surface. Generally, the embeddable layer (usually called overlay) is designed with a thickness close to the lubricant filter threshold. Overlay material property needs a low hardness but on the other hand high ductility and a high elastic modulus to avoid a forcing of the aggressive particles back to the contact. Such a problem is frequently encountered with hyper-elastic materials like elastomer seals.

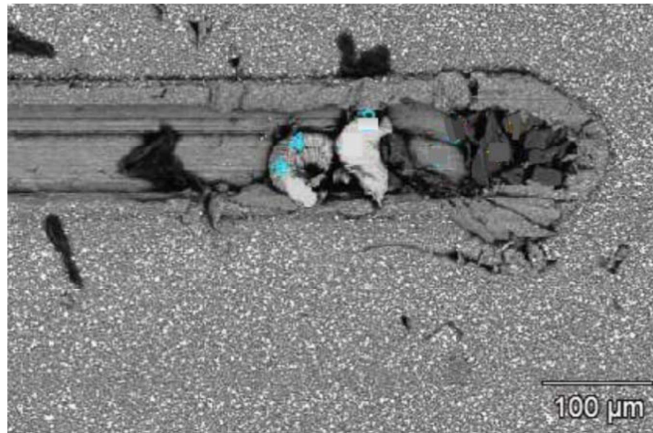


Figure 2 Particle embedded into the aluminium alloy [28]

Conformability

The ability refers to adjustment of bearing in conformal contacts. Bearing material needs to be able to misalign or deform easily between shaft and housing and challenge potential geometric inaccuracies caused by production of parts. Usually, bearing materials that have a low modulus of elasticity (low E) are readily conformable.

Corrosion resistance

Lubricant can represent aggressive conditions in which bearing has to be able to operate. Therefore the bearing material should be resistant to attack by lubricant as well as any other oxidation products produced during lubricant alteration or degradation. In most cases, lubrication oils are composed of additives covering also oxidation inhibitors. In the alteration process of the oil, these additives usually degrade and can produce organic acids, which invade and cause corrosion of certain bearing materials.

Fatigue resistance

The fatigue damages are a complex topic especially when we try to use approach similar to that of the classical material fatigue structural analysis. The overall target of fatigue analysis which is applied to the engine bearing material evaluation is to estimate the cycle number which generates microscopic nucleation in antifriction material.

Figure 3 and Figure 4 represent the three specific fatigue related scenarios based on the differences in materials. Figure 3 represents thick aluminium alloy bearing material where a vertical crack has formed down to the backsteel. It can be seen in Figure 3A that there is a horizontal crack in the adhesion layer to the backsteel as compared to the Figure 3B where no crack in adhesion layer is observed. Adhesion problems not always can be considered the reason. Problems are more complex to evaluate as it can come from several reasons (e.g. heavy load, faulty shape of shaft or housing, etc.)

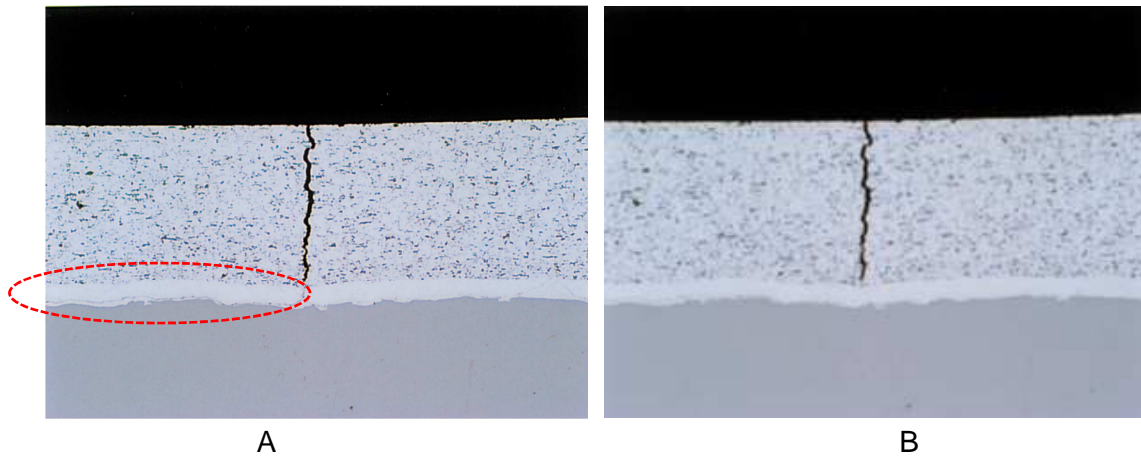


Figure 3 Thick layer with weak (A) and strong (B) bonding [24]

Figure 4 shows a different situation where only thin overlay is depressed, however, no problem is found in the alloy structure.

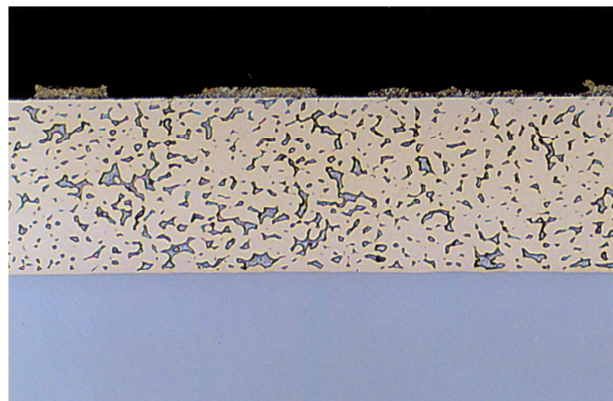


Figure 4 Thin layer fatigue [24]

In combustion engines, frequency and amplitude of loading is changing and depends also on the engine performance. Intensity usually varies cyclically. Fatigue failures can therefore be easily observed initially as cracks in the bearing surface. These cracks propagate usually in the lining of bearing bimetals, interconnecting with other cracks which can be observed. Apart from the loading, high temperature and inhomogeneity of material can cause the damage. This was not the problems of the figures above.

Bearing supplier had to come with simplification of the complexity resulting in an efficient fatigue analysis for bearing materials. They use specific pressure, or diametral pressure as a criterion. It is used formula where radial load F is divided by bearing length L and shaft diameter D .

$$P_{spec} = \frac{F}{LD} \quad (1)$$

Accurate fatigue resistance determination requires advanced measuring involving stress tensors, tridimensional fatigue analysis, using thermo-elasto-hydro-dynamic calculations, etc.

In general point, fatigue testing are expensive methods and therefore calculations usually are in place.

Experimental verification of calculations is done by application tests. Bearing manufacturers use rig tests which involve hydraulics for applying cycling load in high frequency and force until the moment when the crack is identified and measure maximum cycles which the material still can resist.

Wear resistance

Wear is as complex problem as fatigue. It is characterized as “a progressive destructive complex phenomenon which occurs during relative motion of two counteracting surfaces and deterioration of surfaces takes place in industrial operations” [29].

Regarding the bearing, we distinguish also different kind of wear associated with defects on the bearings:

Adhesive wear

During the running is the assurance of lubrication failure almost leading to sliding metals in contact where adhesion followed by wear is generated [30]. Adhesive wear (see Figure 5) is a surface damage and material removal which appears when counterpart smooth surface materials are in contact in an area of oil film breakdown. In these places, high local loading occurs which involves plastic deformations, elevated temperatures and local micro-weldings [31].



Figure 5 Detail of adhesive wear on engine bearing (AlSn20Cu1 alloy) [32]

Adhesive wear can exist as a form of seizure which corresponds to increased temperature even up to the melting point of sliding material. The faster the sliding speeds, the faster the seizure process results in changes of mechanical properties and structure in a range of 0.005 to 0.08 mm. Deeper changes leads to seizure of bearing.

Adhesive wear can be prevented by several measures:

- Precise geometric shape (roundness and roughness influence negatively number of local loading contacts, plastic deformation and temperature – lower possibility of junctions, micro-weldings).
- Counterpart material selection.
- Stability of oil film in boundary regime and formation of boundary layer (e.g. by chemical absorption).

Abrasive wear

When surface is loaded against particles from harder material, an abrasive wear occurs. Hard particles can be formed from counterpart where frictional effect causes ripping of some parts. Source of abrasive wear formation is also in particles attached to the surface of one counterpart and free particles coming to the contact with oil (damaging surfaces of both counterparts). The process is mechanical unless other aggressive conditions are in place. Harder material resist better to abrasive wear. On the other hand, embeddability of material can cause another potential elimination of hard particles. Particles can also be hardened from plastic deformations or oxidation in sliding contact.

The example of abrasive wear evolution is described on the mechanism in Figure 6 where microcuttings and fatigue due to counterbody's hard surface asperities or hard particles in the contact.

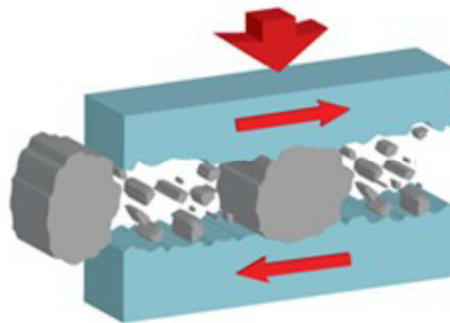


Figure 6 Mechanism of abrasive wear [33]

Tribochemical Reactions

In tribochemical reactions, the chemical reactions take place between the substrate material and counterpart because of the friction-induced activation in the main loaded area near surface zones with elements of the lubricant or ambient medium. Compared with the base body and counterbody, the reaction products exhibit changed properties and, after reaching a certain thickness, can be subjected to brittle chipping or even exhibit properties reducing friction and/or wear.

Seizure

Seizure is a failure of biggest importance for bearing design engineers. Seized bearings cause a serious damage in potential engines and materials and dimensions need to be chosen carefully to avoid it.

Theoretically, seizure occurs when the heat generation is higher than the heat dissipated by heat transfer and by lubricant flow. Practically, from experiences we know that seizure is mostly due to geometrical defects. It happens when the shaft directly contacts the bearing due to the lack of oil, startup, stoppage, uneven contact, etc., and severe overheating or surface flow results in even further heating causing adhesion or seizure. Too low clearance or too high clearance can generate high heat generation in bearings, which can induce seizure.

Illustration in Figure 7 represents the described phenomena. There are two domains of bearing seizure (red on figure) with respect to the clearance and the speed. For a large

clearance, seizure is induced by asperity contact. For a low clearance, seizure is due to clearance reduction by different thermal expansion between the shaft and the housing.

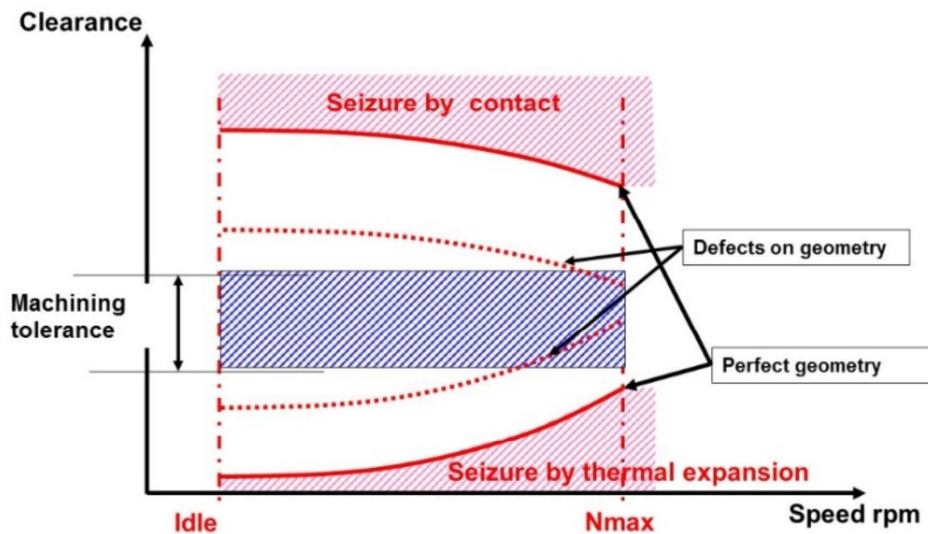


Figure 7 Seizure graph [34]

Bearing surface is machined (often using a process called boring) with some tolerances for the dimensions. The aim is to achieve clearance set by design engineers. Blue part of the graph is the variation for this machining in order to assess the seizure risk with respect to this machining tolerance. Shaft geometry or bearing geometry is not possible to machine perfectly. Therefore, local geometrical defects must also be taken into account to determine the seizure domain limits. The seizure areas will grow with respect to the geometrical defect amplitude. With the help of the red dot lines, it is possible to introduce worse geometrical defects to check if the clearance variation is still in a range to avoid seizure. Imply the blue rectangle must not cross the dotted red lines.

So, for new bearing designs, it is necessary to estimate the friction (mixed and hydrodynamic) for bearings with the largest geometrical defects associated with the bearing and shaft machining quality.

Practical example of improper machining quality of shaft can be seen in the Figure 8 where the seizure is observed around the centre of main bearing. Shaft ran-out and caused stop of the engine.

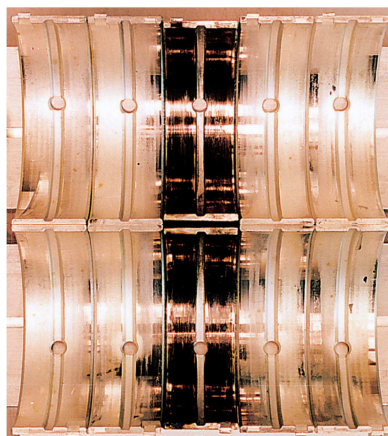


Figure 8 Seizure is observed on the centre of main bearing [24]

Thermal resistance

The thermal characteristics of the bearing material are difficult to approach. It has to be considered with regard to both heat dissipation and thermal distortion. The thermal conductivity is considered high to ensure maximum dissipation of the frictional heat generated in boundary and mixed lubrication regimes and has strong effect on seizure properties.

Further parameter which should be taken into account is linear thermal expansion coefficient. Bearing design has tough tolerances which could result in problematics in temperature variations.

Cavitation resistance

Cavitation erosion damage to bearing surfaces is a form of micro fatigue cracking initiated by the collapse of vapour cavities. Most commonly is observed near the oil hole where the oil enters the contact of bearing with shaft. Usual general knowledge is that lubrication conditions are necessary to change regarding the oil pressure or flow rate.

4.2 Material compositions

The composition of bearing material is usually concern of confidentiality for each bearing producer. Looking at the history of sliding bearings, probably the oldest one was made of wood (wheel connected to wooden housing). Further development especially in driving parts needed revolution in materials. Leonardo da Vinci recommended the tin for bearing [35] and before leaded bearings where the number one used component and still remained until today.

4.2.1 Tin and lead materials

Lead- and Tin base materials (also used to be called babbitts) still belong to the most widely used materials for hydrodynamically lubricated bearings offering perfect surface action between the bearing and journal surfaces. There is minimum damage of a steel journal under boundary lubrication conditions or in dirty lubrication and they exhibit excellent compatibility and anti-seizure characteristics. The softness of surface also provides perfect embeddability and conforms to geometric errors in machine construction and operation. They still have the majority of use as a material regarding engine bearings. Only automotive had to move from using of the lead based materials to the tin-based because of the European regulation (ELV).

It has relatively low load-carrying capacity which the industry solved by metallurgical bonding of these alloys to a stronger backing materials such as steel, cast iron, or bronze.

Babbitt linings are either still cast or centrifugally cast on the backing material. Fatigue strength is increased by decreasing the thickness of the babbitt lining.

Other materials are usually used only when higher load capacity is required and/or system is working under higher-temperature operation and/or requirements for fatigue life are higher than those of babbitt materials.

Regarding fatigue, basic problems have been improved by intermediate layer of a high strength fatigue-resisting material between a steel backing and thin babbitt surface layer. These composite bearings often eliminate the necessity for going to other bearing surfaces with poorer compatibility than is possible with babbitts.

4.2.2 Aluminium alloys

Usage of aluminium alloys in bearing industry is known for a very long time. Decent mechanical properties like anti-seizure, wear resistance, elongation and hardness scored caused massive extension of variety of these alloys in bearing applications. The usual compositions contained tin, copper, nickel and magnesium in different amounts and showed great potential to replace conventional tin base babbitts and leaded bronzes [36]. In the past, lead was cheaper option to tin whereas also more effective soft phase addition needed for aluminium.

Regarding European market, leaded aluminium alloys appeared as a problem as described in the sections above. Moreover conventional melting and casting of leaded alloys also caused some troubles regarding segregation of aluminium and lead phases based on the differences in density especially when the addition of Pb was above 1.5 % [37].

Steel-backed aluminium bearings have been found the biggest potential in crankshaft and big-end bearings in variety of compositional optimisations [38].

4.2.3 Copper alloys

Copper alloy materials for bearing applications can either be cast or wrought. However, the majority of the bearing materials such as high tin phosphor bronzes and leaded bronzes cannot be fabricated because of their special duplex structure, and bearings made from these alloys must be cast. Wrought materials are used where the bearings can be manufactured more economically by fabrication rather than by casting [39].

Bronzes are used in some applications as cast bearings without a steel backing (e.g. thrust washers of floating bearings for turbochargers).

Lead bronzes containing up to 25 % lead, provide higher load-carrying capacity and fatigue resistance and a higher temperature capability than the babbitt alloys. Tin contents up to about 10 % are used to improve the strength properties. Higher-lead bronze (70 % copper, 5 % tin, and 2-5% lead) can be used with soft shafts, but harder shafts (300 BHN) are recommended with the harder lower-lead bronzes, particularly under conditions of sparse lubrication.

Lead bronze bearings are used in pumps, diesel engines, railroad cars, home appliances, and many other applications.

Tin bronzes, which contain 9 to 20 % tin and small quantities of lead (usually < 1 %), are harder than lead bronzes and are therefore used in heavier-duty applications as well as turbocharged engines as the lead-free materials in automotive.

4.3 Production of engine bearings

As described earlier, the material for bearing production has to consist of several layers in according to fulfil the hard conditions in the engine. Production method of material consists of layer of an alloy with the desired characteristics bonded to a steel base (backsteel).

Strong bonding is required for the bimetal so that the steel and alloy layer do not separate after the bearing is mounted in the machine. The steel and alloy are basically attached by the bonding of metallic atoms. Technologies called sintering, roll bonding, and casting are used to attach the backsteel and bearing alloy at the atomic level at high temperature and pressure. One of these three techniques or mechanical bonding is selected according to the alloy type.

4.3.1 Sintering

Sintering is mainly used for copper alloy bimetal. Copper alloy powder is spread on the backsteel and bonded at high temperature. The production scheme is on the figure below (Figure 9).

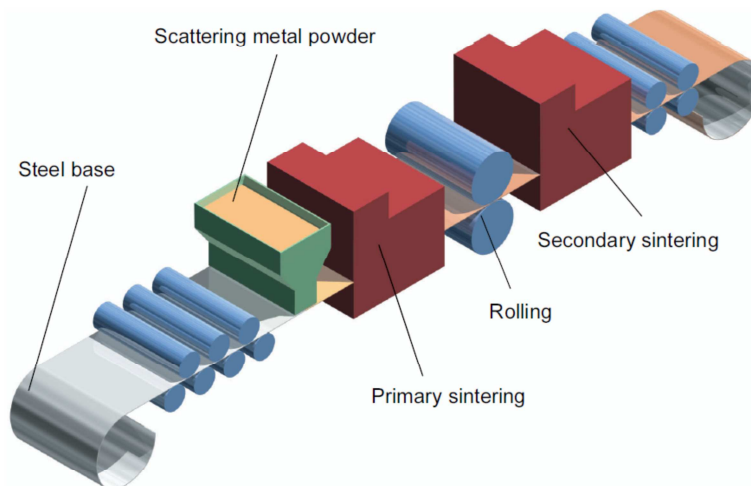


Figure3-4 Sintering process

Figure 9 Sintering process [24]

The basic raw material is bearing steel coil. It usually comes from the steel manufacturer. For the purposes of bearing, usually cold-rolled steel is produced. As from the hot-rolled coil, the cold reduction process produces closer dimensional tolerances which are required for bearing industry.

The steel strip is uncoiled levelled by series of cylinders before metal powder is spread to the surface. Washing of the strip is usually required so the bonding is maintained after the sintering process. Cleaning of steel coil can be done by either hot alkaline solution or mechanically.

The metal powder is added to tray with the prior controlled particle size and material composition quality. Spreading powder requires previous careful calculation based on experiences of necessary alloy thickness. This requires knowing the ratio between the densities of the powder and the sintered ally and elongation of the strip during the rolling.

Sintering process is know-how of each manufacturer. Sintering furnace is a continuous sleeve-type and several meters long where temperature reaches over 800°C depending on the alloy composition and is also result of research and development of bearing manufacturer. The atmosphere in the furnace is also controlled to be reduced. The reducing is necessary to convert all the surfaces of powder particle into the metallic state:



The particles are welded to each other and to the steel strip due to the mutual diffusion of their atoms.

The sintering process needs to be performed twice. Primary sintering to weld particles and bond them to steel coil and then re-sintering to eliminate closed pores formed between the joined particles. Re-sintering is conducted in a sintering furnace similar to that of the sintering stage with similar parameters as well as the process.

The ideal result is sintered structure of the copper alloy without any porosity with a similar structure as below on the picture (see Figure 10).

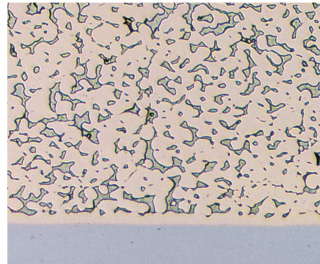


Figure 10 Structure of the Copper alloy [24]

The second phase (can be for example lead, bismuth, tin) is homogeneously distributed throughout the copper based matrix in form of small particles located between the copper grains.

4.3.2 Casting

Casting process is at the beginning same as the sintering process (see Figure 11). Steel coil is straightened and washed in alkaline solution and cleaned mechanically by cylindrical brushes. Strip edges are formed on the sides to keep melted copper alloy and prevent its side leakage.

Steel is preheated to about 1000°C in inert atmosphere preventing possible oxidation and melted copper alloy is poured onto the strip surface. Cooling is done by water.

Finishing process is composed of edge trimming by slitting the strip edges and polishing the surface. The strip is recoiled and follows to the further machining process for bearing production.

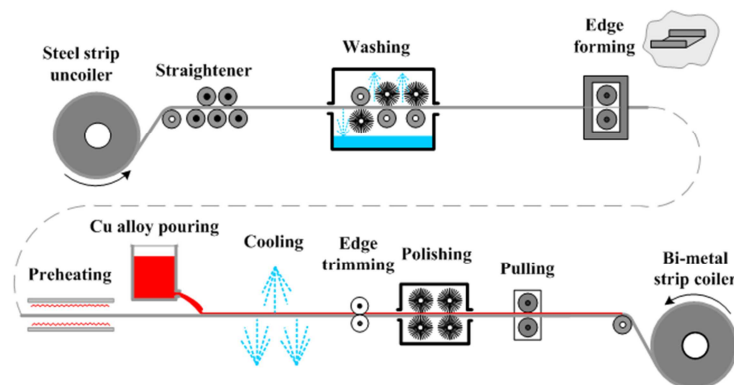


Figure 11 Casting process of copper based bi-metal strips[40]

4.3.3 Rolling process

Rolling process is usually used for aluminium alloy bimetal. The process can be seen in the figure below (see Figure 12).

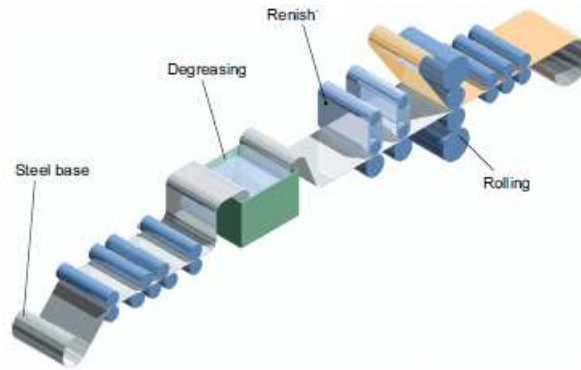


Figure 12 Roll bonding of aluminium bimetal [24]

Degreasing and mechanical cleaning is done for both the steel base and the prepared aluminium strip. Both strips enter rolling mill where they adhere to each other as a result of Solid State Welding. The pressure necessary for achievement of bonding is obtained at relatively high thickness reduction for on-pass rolling operation (4 rolling mills are used for bonding aluminium alloy with steel strip as seen).

4.4 Coatings

Although the material alloys and bimetals have been developed to meet requirements of the tribological properties, the complexity of mechanical and physical properties required coated surfaces as the combination in terms of hardness, elasticity, shear strength, fracture toughness, thermal expansion but especially adhesion to the substrate material.

It generally recognized four zones when applying surfaces where particular each zone must be considered different property (see Figure 13)

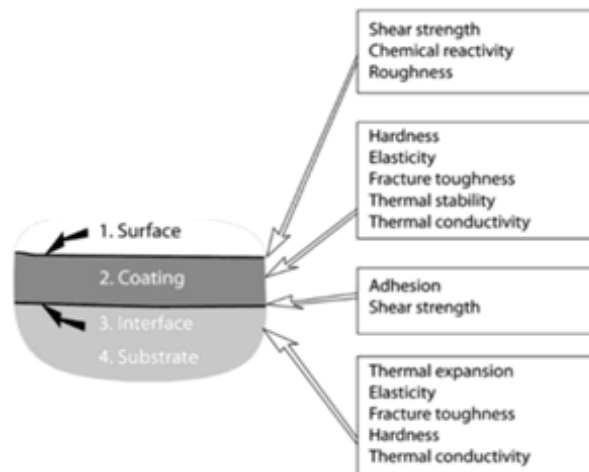


Figure 13 Material properties in different zones of the coated surface [41].

Substrate and coating material properties are generally determined by their composition and microstructure where porosity and homogeneity plays role. At the interphase, the mentioned adhesion and shear strength of the junction is important. The main focus on the surface of the coating is the study of chemical reactivity and surface roughness or preparation of surface artefacts together with the shear strength.

Also the coating design itself undergoes again in compromising of properties, such as good adhesion at the coating/substrate interface and no surface interactions with counterface,

or hardness versus toughness and obviously the cost of the preparation and application of the coating onto the product [21].

Holleck (scheme Figure 14) in his study characterized how aside from material selection, composition and also fabrication parameters determine the microstructure. In this sense the coating system usually represents a sort of composite system and bearings simultaneously benefit from this option as well as they become very dependent on the production.

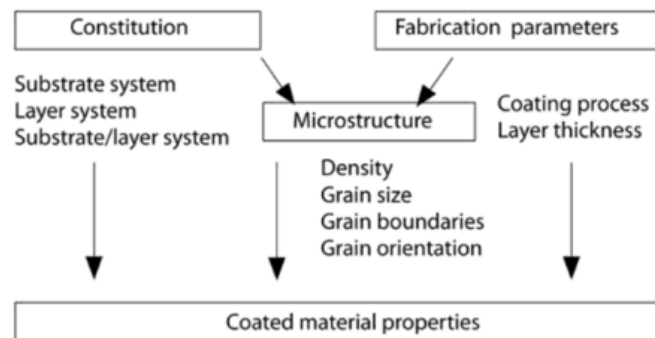


Figure 14 Examples of parameters influencing material properties of coated surfaces [42].

Expansion of tribological coating development started massively especially due to the availability of new coating methods which can control morphology and adhesion properties of coatings which were not available previously. The deposition techniques that have caused most of the interest in this field are primarily plasma and ion based methods.

Rickerby and Matthiew [43] classified the deposition processes into the following four categories:

- Gaseous state processes,
- Solution state processes,
- Molten or semi-molten state processes,
- Solid-state processes.

Solid-state processes are usually connected to thick coating. Therefore it was not gathered in the table (see below Figure 15). Regarding bearings, especially in engine plain bearings there is micrometer level range in which the material engineers can play.

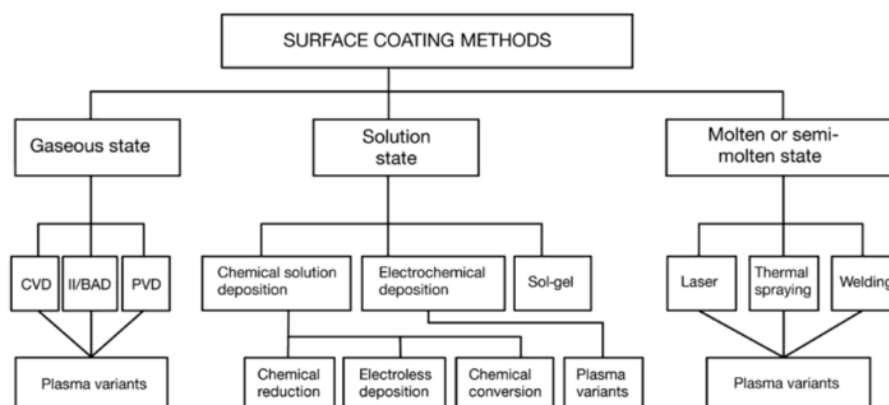


Figure 15 General classification of surface engineering method.

Each process can achieve different range in thickness which plays important role as had been pointed out. Figure 16 represents a scheme of approximate range for the coating thickness according to the technology and how it is vary as well as the deposition temperature. The temperature can influence the substrate material.

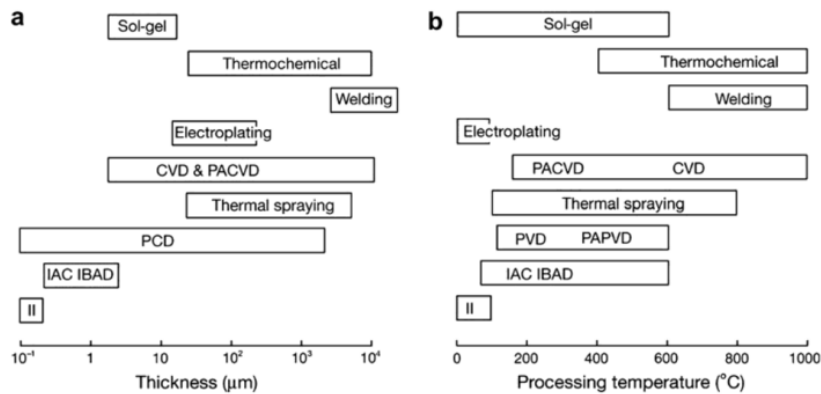


Figure 16 The typical range of coating thickness (a) and processing temperature (b) for coating technologies.

4.4.1 Electrochemical deposition

As requirements for bearing have increased, the functional top layers were introduced and electroplating has become one of the common process used for engine bearings. With Bi-metal bearings where the overlays is absent, tribological performance is determined by the bearing lining itself. There is a limitation to fulfil all the required properties in high loaded conditions.

Electroplated or galvanic coatings are widely used in the form of soft metals and since these overlays are rather thin, they have shortcomings in terms of mechanical strength [44].

Lead based PbSn(8-18)Cu(0-8) system is a commonly used material. These lead-based matrixes are reinforced by Cu and Sn, which form harder particles and improve also corrosion resistance. Additionally for some application, Indium is added to increase the fatigue and wear resistance [45].

When using tin, the diffusion is commonly appearing to the copper substrate from overlay resulting in lower performance of the overlay. Therefore an intermediate layer of Ni is applied between copper alloy lining and overlay [46].

ELV regulation of EU as mentioned earlier forced to implement Sn, Bi and Ag based systems [2]. These soft layers usually lack wear properties and therefore are doped with hard particles [47].

4.4.2 Sputter coating

Sputter bearings were developed already a decade ago to improve load carrying capacity and wear resistance of engine bearings because of turbocharged systems of engines. But the production came more recently. The reason was connected mainly with production scale of deposition processes. Main difficulties were connected to process control and electronic technologies with knowledge of plasma physics and chemistry.

The production technology using physical vapour deposition (PVD) processes commonly employ a method known as sputtering. The technique helps to produce material with fine grained structures. Atoms released from target material by ions, are deposited onto the

substrate material. A typical target material composition for this overlay is AlSn based alloy. The most widely used is the AlSn20 alloy. The deposited formed layers are much harder compared to the target material itself. These sputter coatings possess high fatigue strength, high load carrying capacity and high wear resistance combined with moderate sliding properties [48]. Hence, they find their use in highly loaded turbocharged diesel engines. One of the disadvantages of these coatings is their comparatively high costs. The reason for PVD technique is refinement of microstructure. This refinement influences strongly tribological performance of the layer. Example could be found in the work of Rosa et al. [49] who found the friction coefficient of thin film from AlSn20 deposited by magnetron sputtering which is lower than that of commercial Al–Sn alloy.

The sputter bearings have high fatigue resistance and exhibit high load carrying capacity and high wear resistance and therefore they found their use in highly loaded engine bearings. One of the disadvantages of these coatings is their high costs.

4.5 Polymers in engine bearings

In general, polymeric materials have had the greatest progress among triboelements of recent years and found its way in tribological applications. The main reason is the fact that polymers offer inherent properties such as light weight, ease of manufacturing and corrosion resistance. Moreover, by adding some reinforcements and lubricants they give better tribological properties, which are unreachable with metals, ceramics or neat polymers.

When we look at the engine bearings, it does not have the long term development. It came with introduction of high performance and thermal resistant polymers such as polyamide imide. Polymer based coatings are usually incorporated with solid lubricants predominately used as running-in layers. In certain cases, they are used as permanent layers as well. They are typically sprayed on the bearing surface and these layers improve the running-in behaviour as well as the geometrical adaptability. A widely used matrix material is polyamide-imide (PAI) with MoS₂ and graphite lamellae as filler material. As permanent layers, these composite materials reduce the friction to the rotating shaft when the lubricant film breaks down.

Regarding polymers, we are recognizing two categories: thermosetting and thermoplastic materials. Regarding thermosets, nonoriented fibers are generally set in phenolic resins. Regarding thermoplastics, nylon has been recognized as valuable bearing material aside of low-friction polymer polytetrafluoroethylene (PTFE).

The main focus of polymer overlays for crankshaft and conrod bearings was towards high performance polymers such as polyamide imide (PAI).

4.5.1 Nylon

Nylon has good abrasion resistance, a low wear rate, and good embeddability. Like most plastics, it has good anti-seizure properties. It has low thermal conductivity (0.24 W/m·°C), and failure is usually the result of overheating. Cold flow (creep) under load is one of its main disadvantages. This effect can be minimized by supporting thin nylon liners in metal sleeves. Nylon bearings are used in household applications such as mixers and blenders and for other lightly loaded applications [50].

4.5.2 Polytetrafluorethylene (PTFE)

PTFE is well known polymer in tribology. It exhibits low coefficient of friction in a contact with harder counterpart. The disadvantage is high wear rate which eliminates the application for higher load pressures and surface speeds.

PTFE exhibits poor wear and abrasion resistance, which can lead to early failure [51]. Regarding the bearings, PTFE is usually used as an additive to wear protective matrices in case of bushings. The wear resistance can be increased also by implementing proper fillers [52].

Regarding our work, PTFE has been excluded from study since it was established that PTFE exhibits significantly low coefficient of friction when sliding against steels. The low coefficient of friction results from the ability of its extended chain linear molecules, $-(CF_2-CF_2)_n-$, to form low shear strength films upon its surface and mating counter-faces during sliding [53].

Recently, GGB has patented a sliding layer for production of multilayer self-lubricated bearing based on PTFE [54]. They added 10 to 20 vol. % sphalerite (ZnFeS) as a lubricant which allows the sliding layer to be self-lubricated. Then approximately 10 vol. % secondary lubricant - graphite and antimony oxide is added to improve frictional properties.

Bickle et al. patented⁵⁵ low frictional bearing composite material based on PTFE where they used 10-25 vol. % zinc sulphide with smaller particle size than 1 μm and 1.5-3.5 vol. % carbon fibres and 1-7 vol. % PFA. It is claimed that Zinc sulphide support homogeneous distribution of carbon fibres in the composite. Particles of ZnS are wetting the surface of carbon fibres and which includes bonding of carbon fibres to the PTF substrate material. Carbon fibres are claimed of 10-20 μm and length 100-200 μm and used as additive to decrease friction of resulting material.

4.5.3 Polyether ether ketone (PEEK)

PEEK is a semicrystalline thermoplastic with excellent mechanical and chemical resistance properties that are retained to high temperatures. The processing conditions used to mold PEEK. It can influence the crystallinity, and hence the mechanical properties [56]. It is also common material as a polymer matrix material for several engine bearing manufacturers, especially in the production of bushings.

The real advances in parameters are coming from filling the PEEK matrix by other additives in according to improve the material properties for different application. PEEK itself from the tribological viewpoint has relatively high friction coefficient especially during unlubricated sliding conditions but the wear rates are remarkably low and therefore became popular.

Rodriguez et al. compared the tribological behaviour of solid lubricants in a polyetheretherketone (PEEK) polymer matrix under different contact pressures and sliding speeds on dry reciprocating conditions with a 100Cr6 steel as a countersurface. They have finalized the lowest coefficient of friction was achieved by the PEEK material using PEEK with 10 wt. % of PTFE, 10 wt. % graphite and 10% wt. of short carbon fibres. According to the researchers, the main reason was the self-lubricant effect of PTFE. The formation of a transfer film (secondary layer) was mainly observed by them with neat PEEK where the adhesion provided a protective effect to damage with better wear resistance. They also have observed abrasion with dominant wear mechanism in materials filled short carbon fibers (SCF), PTFE and graphite. Graphite and PTFE are known for reducing adhesion between

polymer materials and steel countersurfaces. This was according to scientists attributed to the soft nature of PTFE which is poorly adhered to the countersurface and is rapidly removed as wear debris [57].

K.A. Laux et. al [58] had investigated what is the surface temperature of PEEK polymers in sliding conditions on steel and sapphire counterparts. As for our case, we are not considering sapphire counterparts in future for engine bearings. Interesting conclusion on the outcome is that the PEEK debris were found adhered to the steel surface as well as iron oxide residue on the PEEK wear scars and this phenomena was not observed on sapphire. The PEEK transfer film on steel countersurface is highly oriented which suggests its formation process is similar to drawing or extrusion of polymers at high temperature. The transfer film formation processes are the one which influence the friction and surface temperature.

Kalin et.al from University of Ljubljana [59] investigated effect of the material type and the morphology of well-known solid lubricant nanoparticles on the tribological properties of PEEK composites. They used WS_2 (Tungsten (IV) sulfide) fullerene-like (WS_2F), WS_2 needle-like (WS_2N), carbon nanotubes (CNT) and graphene nanopowder (GNP).

The WS_2 -based nanoparticles increased the wear performance as classically the carbon based composites are known for as compared to PEEK, WS_2F improved the wear rate by 10% and the WS_2N by 60%, while the carbon-based particles deteriorated the wear behaviour by 20% (CNT) and as much as three times in the case of the GNP. The addition of WS_2F nanoparticles and the CNT resulted in a lower coefficient of friction compared to the WS_2N particles and the GNP. The resulting diagram seems do mistake in description but probably WS_2F is around 0,4 (see Figure 17).

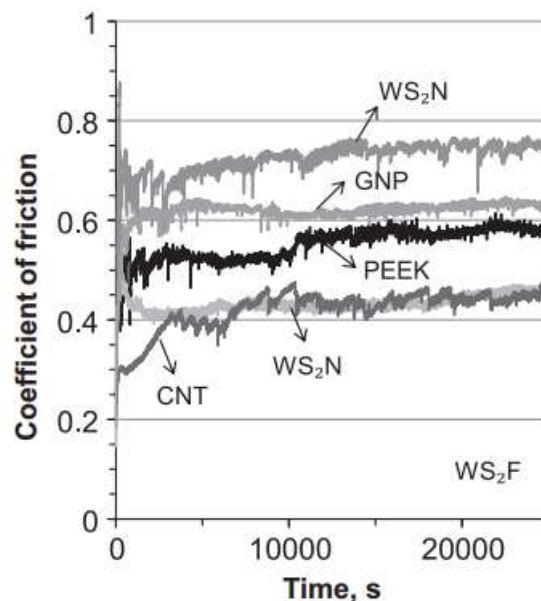


Figure 17 The representative friction–evolution curves as a function of sliding time [59].

One of the main applications of PEEK materials regarding engine bearings are toward bushings used for fuel injection pumps. The lubrication of these elements is rarely reported. Zhang et al. [60] have studied performance of PEEK materials under fuel and engine oil lubrication conditions. Even very small quantity of diesel decreases obviously the friction coefficient and wear rate of pure PEEK. The same was observed with PEEK filled with multiple fillers, i.e. short carbon fibers, solid lubricants and ceramic particles. They believed

that tribofilm produced with diesel lubrication block the material transfer of solid lubricants towards the surface of PEEK and any other tribolayer formation on the surface of bearing. Therefore the frictional results for dry conditions and lubricated are of the significant difference (see Figure 18).

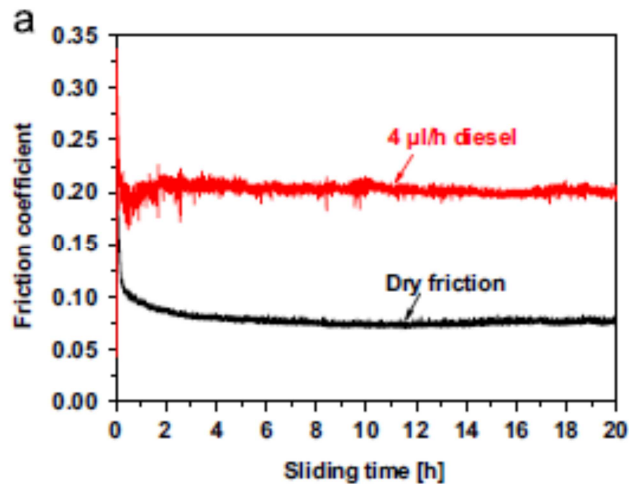


Figure 18 Friction coefficient evolutions of PEEK-Com under dry friction condition and with 4 μL/h diesel “lubrication” [60].

4.5.4 Polyamide-imide (PAI)

Polyamide-imide (PAI) has been commercially available for several decades. The synthesis, properties and applications have been extensively described in past in a similar attractively as polyamides and polyimides. Their superior mechanical, thermal and oxidative properties have made them suitable for various applications [61] and therefore have found the interest also in engine bearing producers.

Although PAI is an amorphous thermoplastic, it requires a post cure after application to surfaces in order to increase its molecular weight, which increases the chemical and thermal stabilities of PAI. The chemical degradation of PAI matrix can be created only by hot steam and high pH. The neat PAI’s compressive strength and its impact strength are higher compared to other high-performance polymers (see Table 1).

Table 1 Comparison of the Compressive Properties and the Impact Strengths of Selected High-Temperature Thermoplastics

| | Compressive Strength (MPa) | Compressive Modulus (GPa) | Impact Strength (Izod, Notched) (Jcm ⁻¹) |
|--------------------------|----------------------------|---------------------------|--|
| Torlon 4203 (PAI) | 166 | 3.3 | 1.06 |
| Temppalux PEI | 151 | 3.3 | 0.53 |
| Techtron PPS | 148 | 3.0 | 0.23 |
| Ketron PEEK | 138 | 3.5 | 0.53 |

At the beginning, the PAI have been developed as an alternative material to polyimides and polyamides to keep the balance of thermal stability with good processability. PAIs combine the superior mechanical properties associated with the amide group, and the high thermal stability of the imide ring in the same material, thus making the material even

stronger. In addition, the synthetic route to PAIs offers the possibility of incorporating specific functionalities between the amide and imide groups. It was found that synthetic modification of PAIs by addition of flexible linkages or by incorporation of variety of functional groups reduces the crystallinity and enhances the solubility of the polymers [62]. Some example of the list is below:

- fluorene, phthalide or phthalimidine group [63],
- cinnamoyl and azobenzene [64],
- phenoxy phenylene [65],
- methoxy-substituted triphenylamine [66],
- oligoether spacers or bulky pendent groups [67].

The first successful result of PAI synthesis forming into patent was probably the one by Frosch [68]. His synthesis was based on the reaction of 1,2,3-benzenetricarboxylic acid and aliphatic diamines. The reaction was firstly formed polyamic acid, then by thermal cyclization they formed PAI. The thermal stability of these polymers was lower due to the aliphatic diamine precursors which resulted in commercial unattractiveness. The main start was due to DuPont with development of aromatic PAIs around the end of Second World War (therefore references are missing).

Later in seventies, Amoco Chemicals produced Torlon from trimellitic anhydride chloride (TMAc) and 4,4'-diaminodiphenylmethane [69]. The polymer exhibited very high strength, stiffness, creep resistance and displayed good performances at moderately high temperatures. They followed in development. Since then, a lot of chemical and structural modifications have been done on Torlon resulting in spread portfolio of products. Till today, it still remains one of the well-established commercially available PAIs and therefore it was also chosen for this thesis.

The Solvay Advanced Polymers L.L.C is currently manufacturer and trademark owner of Torlon polymers. Torlon® PAI (polyamide-imide) combines the unique performance of thermoset polyimides with the melt-processing advantage of thermoplastic PA. In general, they produce 2 categories of polymer grades:

1. Wear-resistance grades which offers unsurpassed performance in both dry and lubricated environments.
2. High-strength grades retain their toughness, high strength and high stiffness up to 275 °C, making PAI the industry's highest performing thermoplastic. Its broad chemical resistance includes strong acids and most organics.

The resulting comparison diagram of the Torlon PAIs is in Figure 19 below.

The real advantage of the polymer and its use for bearing application is high creep resistance and an extremely low coefficient of linear thermal expansion (CLTE) resulting in excellent dimensional stability. This is important for the bearing industry where micrometer precision is required.

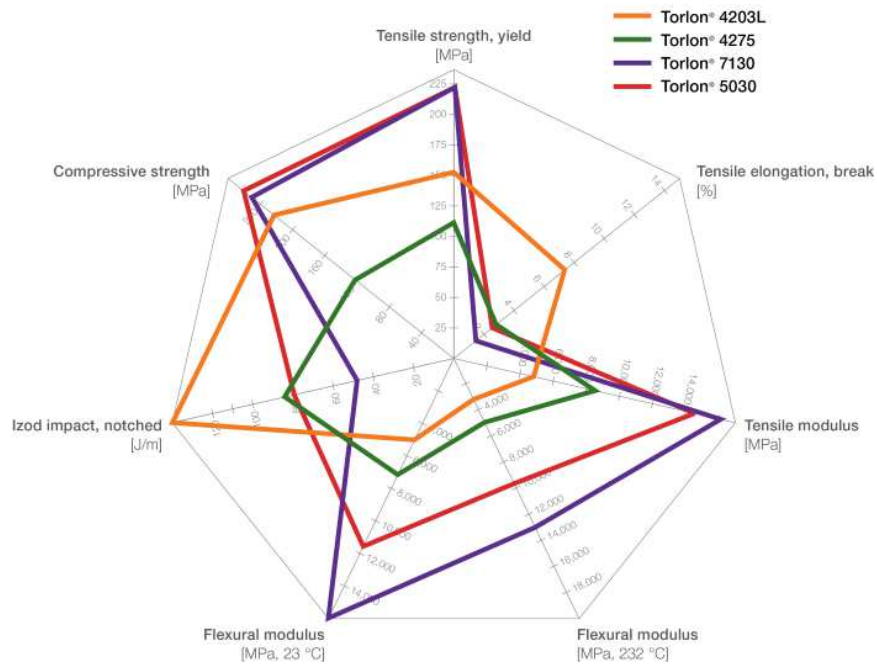


Figure 19 Comparison of Torlon® PAI grades [70]

Torlon PAIs are generally used for molding and all the grades above are also used for it. The tensile strength and tensile modulus of high-strength grade Torlon 4203 reach 152 MPa and 4.48 GPa, respectively. The tensile strength of Torlon 5030 and Torlon 7130 grades, which are glass-fiber and carbon-fiber PAI composites, respectively, reaches 221 MPa. The high-strength grades retain their toughness and strength up to 275 °C which makes them suitable for engine applications.

Applications

A wide range of PAIs have been investigated for applications in filtration, high temperature adhesives, electronic wire enamels, injection-molding techniques, integrated optics and biomedical applications [63–68].

Already several research with application of PAI has been implemented in past. Chitose et al. from Taiho Kogyo company [71] presented a concept of the bearing based on the PAI with MoS₂ solid lubricant. They have achieved 40% less coefficient of friction, 25% less starting torque and 65% less bearing wear in comparison to the conventional aluminium alloy bimetal bearing without overlay under close to the start-stop lubrication conditions by testers.

The testing was done using ball on plate test as well as bearing tester with static loading conditions mainly for wear and frictional results.

Shabanian et al. from Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute in Iran [72] implemented new composite based on a semi-aromatic polyamide (PA) reinforced by multiwall carbon nanotubes (CNTs) was prepared by a solution mixing method. PA was synthesized through a direct polycondensation between azelaic acid and bis(3-amino phenyl)phenyl phosphine oxide. The effect of the CNT addition was mainly for the flame retardancy.

Gebretsadik et.al. from the Luleå University of Technology [73] looked at the Pb-free bearing materials in according to study them and compare the friction and wear behaviour

under mixed and boundary lubrication conditions. The friction and wear evaluation was performed using block-on-ring test configuration. Different rotational speed was used for investigation running-in friction in mixed and boundary lubrication regimes for these materials. Also longer tests were used for state-friction behaviour and wear characteristic results. The findings show a positive effect of PAI based overlay containing MoS₂ and graphite especially at lower sliding speed where has better wear resistance than Pb-based and Al-Sn based materials.

Recently, Federal Mogul company released application for patent of sliding coating based on PAI to piston rings as well (their well-known application of this coating is for engine half bearings as mentioned before). The additives are ferrous oxides with MoS₂ or other solid lubricants for mainly wear and anti-seizure modifier of the coating [74].

Daido Metal company leads also several patents over the world relating to the PAI base overlays. In USA, they patented [75] the composite layer based on PAI with addition of solid lubricant based on PTFE and MoS₂ for lowering the frictional abilities together with hard particles based on metal oxides for increasing in wear. According to their knowledge, less than 1 wt % of the hard particles cannot improve the wear resistance. On the other hand, if the hard particles are more than 50 wt %, the coating layer is oppositely worse in wear resistance.

According to the invention, the polyamide used for the realization of the sliding surfaces may be advantageously crosslinked, e.g. chemically or by irradiation, thus allowing to increase its maximum operating temperature, mechanical strength and modulus of elasticity compared to the a polyamide that is not crosslinked. Crosslinking of the material also allows to obtain a higher surface hardness and to increase wear resistance and dimensional stability in view of high operating temperatures.

Fortune Construction Engineering Ltd. patented the low-friction polymer material based on cast polyamide 6 which they crosslinked with lubricants on a liquid state thus allowing to keep good frictional properties and increased mechanical properties, especially compression resistance in compare to the fluoropolymers. The crosslinking allowed to increase the molecular weight of the polymer and to form the intermolecular bond which can further influence the material properties [76].

A composite material for sliding surface bearings based on the aromatic polyamide fibers (0.02 to 0.1 mm in diameter and have a length of ≤ 0.3 mm in a volume ratio 1.5 to 15%) was claimed in US patent US4847135 A of Kolbenschmidt Aktiengesellschaft [77] where as the matrix they used a polymer selected from the group consisting of polytetrafluoroethylene, polyvinylidene fluoride, polyethersulfone, polyetheretherketone, polyetherimide, polyphenylenesulfide, polyacetal and polyimide in volume ratio 5 to 35 % and in mixture of the two of them.

Miba Gleitlager Austria patented [78] sliding layer based on PAI of 60-80 vol. %. Molybdenum sulfide (15-25%) and graphite (5-15%) used as an additive for frictional properties. The proportion of polyimide resin was preferably calculated for the amount of solvent to be removed. The disadvantage of this solution was mainly in strength and possible use in highly loaded plain bearings. Therefore they recently patented [79] sliding layer composed of the PAI based with the same solid lubricant particles as in previous patent but with mixture of alumina powder. They claim that further improvement in wear performances of the surface layer, hexagonal boron nitride was used in the range of 5-25 %.

Another similar structural bearing material as for the layer was patented by Mahle [80]. The cross-sectional image of the bearing material is on Figure 20.

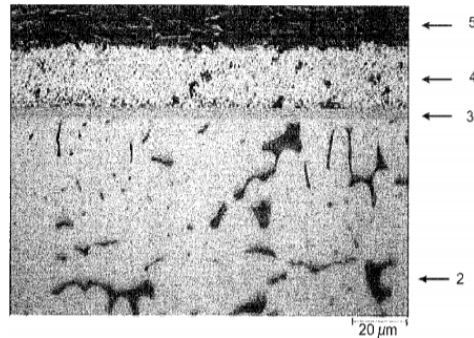


Figure 20 Sliding bearing patented composite

The base material is bearing steel onto which applies a primary layer of bronze alloy (2) with composition of 4-8 % tin, 1-4 % bismuth, 1-3 % nickel with balance to copper in thickness 150-400 μm . They claim that in accordance with sputter the layer (4), the bonding layer has to be implemented (3) to increase the bonding forces. The bonding layer comprises nickel and chromium in a range of thickness 1-5 μm . The sputtered layer (4) comprises 1-40 % tin, 1 % silicon, 1% copper, 2% iron with balanced aluminium in thickness 3-20 μm .

The sliding polymeric layer (5) based on PAI matrix provided with a 1-14 % of soft metal (aluminium powder – 5 μm particle size), 5.7 % fluoropolymer (PTFE or fluorinated ethylene-propylene) mainly for lubrication properties and 4.8 % silane-based material.

Silane material (as claimed gamma-aminopropyltriethoxy-silane) was used as a material to increase stability of matrix. Further important function is in adhesion properties to the sputtered layer, as claimed in the patent. The multilayer system exceeded the load capacity 150 MPa which makes it interesting for potential high loaded engine systems. There is obviously also significantly higher cost as compared to classical bearing systems.

Synthesis of PAIs

Synthesis and chemistry of PAIs itself is complicated covering a large variety of existing monomers such as anhydrides, carboxylic acids, diacyl chlorides and diamines, and diverse procedures. The physical, chemical and mechanical properties of these materials can be adjusted or modified by changes in the chemical structure of the monomers or the reaction conditions. Several approaches have been successfully applied for the preparation of PAIs [81,82].

One of the oldest approaches for the synthesis of high molecular weight PAIs is the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by phosphorylation which was introduced by Yamazaki et al. [83] in 1975. Later, this method was successfully modified by many researchers [84, 85].

The most convenient way is synthesis by:

- amide-imide forming reactions,
- reactions involving amide or imide-containing monomers.

Amide-imide forming reaction

This forming method produces PAI by reacting trimellitic anhydride (TMA) or trimellitic anhydride chloride (TMAc) with diamine [86] or with diisocyanate [87].

Avella et al. [88] modified the PAI synthesis and by the direct polycondensation of flexible aromatic diamines with monoesters of isomeric tricarboxylic acid anhydrides with aryloxy group or with monoesters of TMA (see Figure 21) in a single pot system. The method uses triphenylphosphite (TPP) and pyridine as condensing agents to form amide bonds from aromatic diamines and a mixture of isomeric 1,2,4-benzenetricarboxylic acid monoethyl esters. They claimed that these polymers exhibited higher thermal stability compared to those derived from TMA.

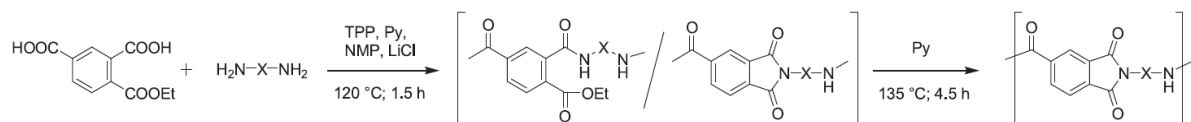


Figure 21 Two-step polymerisation method for synthesis of PAIs by single-pot.

The above methods for PAIs synthesis are producing viscous polyamic acid as an intermediate. Water is released as the by-product during the imidization of the polyamic acid. It results in low yields of polymers (hydrolysis of the polyamic acid). Its synthesis requires very pure monomers and extremely anhydrous reaction conditions to achieve high molecular weights. To overcome these drawbacks, many research groups used diisocyanates as a substitute for diamines. The diisocyanates evolving CO_2 gas bubbles out of the reaction system during polymerization process more easily but reactivity of ANCO group makes the pot life of diisocyanate very short which complicates the whole reaction.

Reactions involving imide or amide-containing monomers

Synthesis where imide-containing monomers are used, a diimide dicarboxylic acid (DIDA) or imide-containing dicarboxylic acids reacts with various diamines to synthesize a series of PAIs. Alternatively, imide- or diimide-containing dicarboxylic acid chlorides can be used instead of the acids. This synthesis has several advantages compared to the conventional polyamic acid type. The final polymers are linear, soluble, and as most important, high molecular weight.

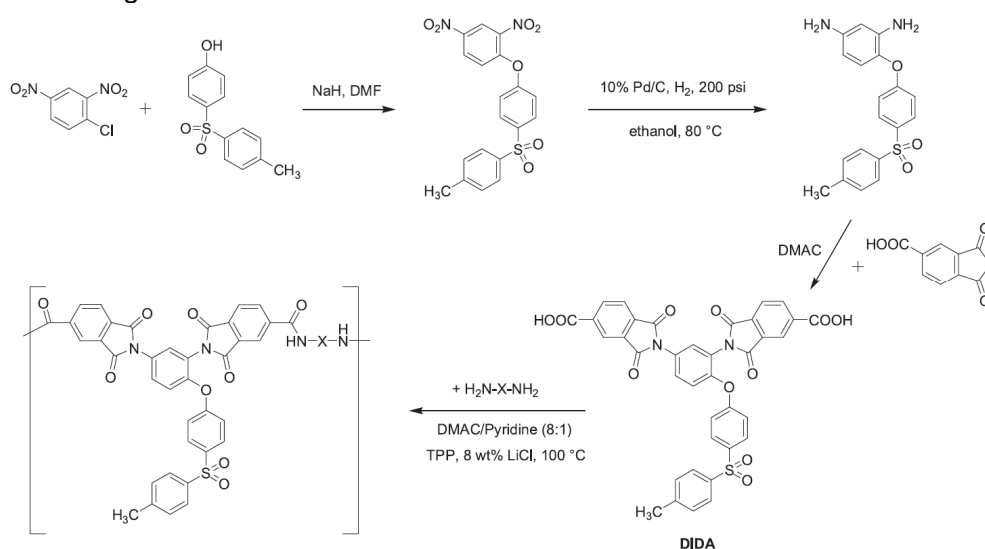


Figure 22 Synthesis of PAI from diimide dicarboxylic acid.

Good example of this work is from Patil et al. from 2007 [89]. They used 4-{4-[(4-vinylphenyl) sulphonyl]}-1,3-bis-trimellitoimido benzene containing sulfone and bulky pendent group as a PAI building block. They obtained high-molecular-weight polymers by direct polycondensation of the DIDA with various diamines by means of triphenyl phosphite (TPP) and pyridine (see Figure 22).

Lately, a lot of novel techniques of production has been developed (microwave irradiation, sol-gel process, ultrasonic irradiation method, chemical crosslinking, etc.). These methods and other PAI synthesis options were not studied since the synthesis of PAI was not part of the thesis. On the other hand, it is evident that there had been a significant progress in designing the structure of PAIs, their precursors, and developing new preparation/modification methods, to improve their thermo-mechanical properties as well as processibility. Interest for PAI is growing due to their high performance polymer properties.

4.5.5 Other polymers

Dixon Corporation patented [90] a composition combining PTFE resin and polyimide resin which can be shaped into the bearing bushing with exceptional resistance to frictional wear and hence which is satisfactory as a dry bearing material even against soft metals. They claim that the co-polymer has unusual synergistic behaviour especially because neither the component alone, neither PTFE resin or polyimide resin, has satisfactory bearing resistance when moving against a soft metal such as brass. Thus, their invention also provides a method of increasing the abrasion resistance of PTFE resins.

4.5.6 Additives in polymers

Nanoparticles

It has been generally accepted that smaller particles have better performance than larger particles in improving the tribological properties of polymers under sliding wear conditions [91], especially in a nanoscale. There was variety of work to verify the theory of polymer nanocomposites.

Rong et al. studied TiO₂ nanoparticles and mainly their distribution effect on wear resistance of epoxy resin matrix when sliding against smooth steel nanocomposite [92]. Xue et al. [93] studied SiC particles in PEEK where the comparison of the dimensions of SiC particles influence the friction and wear of the PEEK composites. He found out that the wear rate of PEEK filled with 10.0 wt.% nanosized whisker SiC was almost unaffected.

The performance of nanocomposites is normally attributed to the large interface area between nanoparticles and the polymer matrix, which potentially leads to better bonding between different phases, and therefore to a better property profile than that achieved with conventional polymer composite [94]. Researches have demonstrated that inorganic nanoparticles can simultaneously improve different mechanical properties of polymer composites, whereas traditional micro-sized particles normally increase some properties, e.g. stiffness, but may have a detrimental effect on others, e.g. toughness and strength [9–11].

Toshihiro Kobayashi et.al patented [95] an addition of vitreous carbon as the additive which can increase tribological properties of conventional bearing material composites. Further, when carbon is blended to the plastic, the manufacturing cost can be reduced as well as weight. Bearing material has less wear, long life, no risk of seizure, improved slidability and heat resistance, and less dimensional changes due to temperature change.

Company Taiho Kogyo patented [96] resin overlay with solid lubricant (MoS₂, PTFE, graphite, WS₂, h-BN, and B₂O₃) with hard material (such as SiC, Al₂O₃, TiN, AlN, CrO₂, Si₃N₄, ZrO₂, and P) in resin which can again vary (PAI and PI resin, an epoxy resin, a phenolic resin, a polyacetal resin, a polyetheretherketone resin, or a polyphenylene sulfide resin).

Different concept was released recently when company Mahle implemented and patented idea of polymer overlay for start-stop application [97]. They described 2 layer polymer overlay for enhanced seizure and scuff resistance under boundary lubrication conditions where both layers have the same composition but different curing temperatures. Matrix was based on polyamide/imide resin, acrylate resin, epoxy resin, phenolic resin or fluoropolymer with dry lubricant as fluoropolymer, Mo₂S, or graphene.

First polymer layer curing at 190 - 240 degrees provided enhanced load carrying capacity and second polymer layer as top layer was cured at 120-180 degrees provided enhanced resistance to seizure and scuffing [98].

Very recently, Federal Mogul applied for the patent [99] where invention is related to the anti-friction coating based on PAI with zinc sulphide and barium sulfate as additives. They claim that tribological properties (specifically load carrying capacity and wear resistance) are significantly improved compare to those containing either only zinc sulfide or barium sulfate. According to their results, the peak load capacity at the crankshaft bearings could be increased up to 120 MPa. This is a value which otherwise is achieved only by aluminum-based sputter coatings.

As the application was used crankshaft bearing where they claim that mixture increase effectivity of lubricant film whereby the increase of the wear rate with the specific bearing load is reduced. This increases the load limit, which in turn significantly increases the operational reliability of the bearing at load beneath the load limit.

4.5.7 Calcium hydroxide

The thesis focuses on the addition of calcium hydroxide to the PAI matrix. There are no literature records on the addition of calcium hydroxide to the polymer. The original idea is coming from generally published articles where inorganic clay minerals consisting of layered silicates in polymer matrices helped with significant improvement on mechanical properties [100, 101]. It was showed that stiffness or Young's modulus can be improved by adding either micro- or nano-particles since rigid inorganic particles generally have a much higher stiffness than polymer matrices [102,103].

It is generally known that the mechanical properties of particulate–polymer composites depend strongly on the particle size, particle–matrix interface adhesion and particle loading [104]. Particle size has a certain effect on the mechanical properties. As an example connected to the baseline coating material, smaller calcium carbonate particles provide higher strength. Smaller particle size of CaCO₃ yields also higher fracture toughness for calcium carbonate filled high density polyethylene (HDPE) [105]. Particle–matrix interface adhesion and particle loading are two important factors that also affect mechanical properties [106].

Regarding Ca(OH)₂, it can be formed of different particle sizes and shapes. For this work was considered the hexagonal plates which can be found in cement paste usually with needles of ettringite [107]. The formation could play significant role as a laminate filler in the matrix of PAI and increase the toughness of the surface.

5 EXPERIMENTAL

Part of Experimental and results are available in the library of Faculty of Chemistry, Brno University of Technology.

6 LIST OF ABBREVIATIONS

| | |
|---------------------|---|
| BoR | Block-on-ring |
| CaCO ₃ | Calcium carbonate |
| Ca(OH) ₂ | Calcium hydroxide |
| CID | Collision induced dissociation |
| CNT | Carbon nanotubes |
| DIDA | Diimide dicarboxylic acid |
| E | Modulus of elasticity |
| EDX | Energy-dispersive X-ray spectroscopy |
| FTIR | Fourier transform infrared spectroscopy |
| GNP | Graphene nanopowder |
| HD | Hydrodynamic |
| ICP-OES | Inductively coupled plasma atomic emission spectroscopy |
| LDI | Laser desorption ionization |
| MALDI | Matrix-assisted laser desorption/ionization |
| MoS ₂ | Molybdenum disulphide |
| MS | Mass spectrometry |
| MTM | Mini-traction-machine |
| NN | Neutralization number |
| NMP | N-methyl pyrrolidone |
| ODA | 4,4'-oxydianiline |
| PAI | Polyamide-imide |
| PVD | Physical Vapour Deposition |
| PEEK | Polyether ether ketone |
| PTFE | Polytetrafluoroethylene |
| RPM | Rotation per minute |
| SCF | Short Carbon Fiber |
| SEM | Scanning electron microscope |
| TBN | Total Base Number |
| TMA | Trimellitic anhydride |
| TMAc | Trimellitic anhydride chloride |
| TPP | Triphenyl phosphite |
| VI | Viscosity index |
| WS ₂ | Tungsten (IV) sulphide |
| WS ₂ F | Tungsten (IV) sulphide fullerene-like |
| WS ₂ N | Tungsten (IV) sulphide needle-like |
| XPS | X-ray photoelectron spectroscopy |
| ZDDP | Zinc dithiophosphate |

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