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# The mechanical strength of phosphates under friction-induced cross-linking

**Z. Pawlak [a,b,*], P.K.D.V. Yarlagadda [a], R. Frost [a], D. Hargreaves [a]**
[a] Queensland University of Technology, School of Engineering Systems, GPO Box 2434 Brisbane, Q 4001, Australia
[b] University of Technology and Engineering, 85-326 Bydgoszcz, Poland
* Corresponding author: E-mail address: zpawlak@xmission.com

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**Properties**

## ABSTRACT

**Purpose:** In the present study, we consider mechanical properties of phosphate glasses under high temperature-induced and under friction-induced cross-linking, which enhance the modulus of elasticity.

**Design/methodology/approach:** Two nanomechanical properties are evaluated, the first parameter is the modulus of elasticity (E) (or Young's modulus) and the second parameter is the hardness (H). Zinc meta-, pyro - and orthophosphates were recognized as amorphous-colloidal nanoparticles were synthesized under laboratory conditions and showed antiwear properties in engine oil.

**Findings:** Young's modulus of the phosphate glasses formed under high temperature was in the 60-89 GPa range. For phosphate tribofilm formed under friction hardness and the Young's modulus were in the range of 2-10 GPa and 40-215 GPa, respectively. The degree of cross-linking during friction is provided by internal pressure of about 600 MPa and temperature close to 1000°C enhancing mechanical properties by factor of 3 (see Fig 1).

**Research limitations/implications:** The addition of iron or aluminum ions to phosphate glasses under high temperature - and friction-induced amorphization of zinc metaphosphate and pyrophosphate tends to provide more cross-linking and mechanically stronger structures. Iron and aluminum ($FeO_4$ or $AlO_4$ units), incorporated into phosphate structure as network formers, contribute to the anion network bonding by converting the P=O bonds into bridging oxygen. Future work should consider on development of new of materials prepared by sol-gel processes, eg., zinc (II)-silicic acid.

**Originality/value:** This paper analyses the friction pressure-induced and temperature–induced the two factors lead phosphate tribofilm glasses to chemically advanced glass structures, which may enhance the wear inhibition. Adding the coordinating ions alters the pressure at which cross-linking occurs and increases the antiwear properties of the surface material significantly

**Keywords:** Mechanical properties; Phosphate; Friction-induced cross-linking

## 1. Introduction

Phosphate glasses are potential candidates for many technological applications, e.g., in optical data transmission, solid-state batteries, sensing and laser technology, nuclear technology, and auto-industry. Their properties such as low melting point, high thermal expansion, mechanical and thermal stress, high chemical durability and aqueous corrosion resistance have been reported.

Better understanding of the mechanical properties of phosphate glasses could lead to broader applications by improving composition of glasses [1, 2, 3, 4].

Some phosphate glasses with no monovalent ions, and with the of di- and trivalent oxides (iron pyrophosphate and Zn-Al-metaphosphate) have Young's modulus (70-80 GPa) and tensile strength (S ~ 6 GPa) [5-10]

It was experimentally confirmed that the addition of metal oxides, e.g., SnO, PbO, ZnO, $Fe_2O_3$ and $Al_2O_3$, results in formation of Sn-O-P, Pb-O-P, Zn-O-P, Fe-O-P and Al-O-P bonds and leads to dramatic improvements in the mechanical properties [1, 5, 11] and in chemical durability of the modified phosphate glasses [12]

Phosphorus compounds under high temperature and friction-induced cross-linking undergo the structural transformation from solid system to amorphous state [13-17]. The friction-induced activation processes of metallic surface in the presence of Fe(II) form a mixed iron/zinc orthopolyphosphate glass layer, $Fe_2Zn(PO_4)_2$. The tribofilm forms antiwear pads in contacting-rubbing areas of surfaces [18-23].

In the present study, we have considered properties of phosphate glasses and phosphate tribofilm glasses under high temperature- and friction-induced cross-linking conditions. Two nanomechanical properties of phosphate glasses and phosphate tribofilms are evaluated. The first one is the modulus of elasticity (E) (or Young's modulus), which is proportional to the force required to deform a sample elastically. The second parameter is hardness (H), which is a measure of material's resistance to plastic flow.

## 2. Mechanical properties of phosphate glasses under temperature-induced cross-linking processes

The zinc-iron-aluminum-phosphate glasses were prepared by melting homogeneous mixtures of reagent at temperatures between 1000–1200 $^oC$. Young's modulus [24] of the phosphate glasses is in the 37-89 GPa range, the value for the iron phosphate glass $Na_2O$-$Fe_2O_3$-$P_2O_5$ is 69.5 GPa. The iron free glasses Na $PO_3$, Zn $(PO_3)_2$, Na-Al-P have the lowest modulus of 35.7, 42 and 60 GPa, respectively. Young's modulus for the Na-Al-Fe-P and Na-Fe-P fibers increased to 68 and 69 GPa, respectively.Young's modulus of the Zn-Al-Fe-P glasses appears to be higher than that of Na-Al-Fe-P glasses had the highest modulus modulus at 89 GPa [1, 5]. The mechanical strength of phosphate glasses of Young's modulus are compared with phosphate tribofilms generated during friction-induced processes, the comparison is presented in Figure 1.

Various structure studies of $Zn(PO_3)_2$ glasses indicate that the what Zn coordination is intermediate, between four-coordinated and six-coordinated and has a very large degree of cross-linking incorporated into phosphate structure as a network formers and contribute to the anion network bonding by converting the P=O bonds into bridging oxygen.

The tensile strength [25] of the phosphate glasses falls into two categories. The Zn-Al-Fe-P glass has a tensile strength in the 4.2-7.2 GPa range while the tenstile strength of the Na-Al-Fe-P fibers is in the range 2.8-4.2 GPa. A similar increase in tensile strength is observed for a $Zn(PO_3)_2$ (2.4 GPa) compared to that of $NaPO_3$ glass (1.8 GPa). This increase in strength is believed to be due to the replacement of monovalent sodium ions by divalent zinc ion, which increases the cross-link density structure and makes the glass stronger. Zinc aluminophosphate (Zn-Al-P) glasses have a higher tensile strength than the zinc iron phosphate (Zn-Fe-P) glasses.

## 3. Mechanical properties of phosphate tribofilm under friction-induced cross-linking processes

Two nanomechanical properties of phosphate tribofilms under friction-induced cross-linking are evaluated. The first one is the modulus of elasticity (E) (or Young's modulus). The second parameter is hardness (H). Recently, nanoindentation methods and spectroscopic techniques have been used to determine mechanical properties of the tribofilm. The addition of iron or aluminum ions to phosphate tribofilms tends to provide more cross-linking and mechanically stronger phosphate structure [11, 27, 28, 29].

Mechanical properties of zinc phosphate tribofilm showed that hardness (2 – 10 GPa) [23, 39, 46] and Young's modulus are thickness-dependent [28]. The Young's modulus values obtained for large and small antiwear pads are in the range of 30-215 GPa [23, 30, 33, 34, 39, 44, 45, 46].

The formation of the highly cross-linked network increased the mechanical hardness coordinated to nearby oxygen ions, they can increase the cross-linking in the glasses structure and thus increase its strength [1, 13, 26, 40].

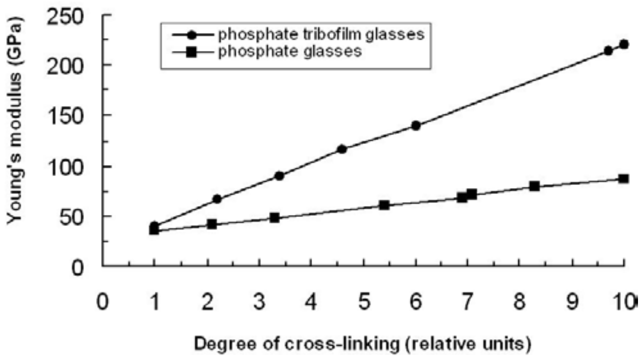


Fig. 1. The Young's modulus of the phosphate tribofilms and phosphate glasses as a function of degree of cross-linking (DCL)

The tribofilm should possess a high hardness to Young's modulus ratio, and value should be far less than that of steel [31]. The literature value of Young's modulus for steel is 220 GPa [32]. The measured Young's modulus value for the ridge region, which corresponds to glassy material, was 81 GPa [33].

Mechanical properties testing with an interfacial force microscope (IFM) revealed that the elastic modulus and hardness of the elevated flat regions differed significantly from the surrounding areas. The Young's modulus of tribochemical films derived from zinc dialkyl- and diaryl-, dithiophosphates has been determined as: 87 and 50 GPa for large antiwear pads, respectively, and 209 GPa for the highly loaded the center region of the pad for ZDDP tribofilm [34].

The Young's modulus values for the phosphate tribofilm glasses and phosphate glasses as a function of degree of cross-linking (DCL) are shown in Fig.1. The representation of Young's modulus against values of DCL was plotted on scale from 1 to 10. For phosphate glasses lowest modulus has sodium phosphate value, $NaPO_3$ = 35.7 GPa (for DCL = 1) and serves as a starting point. Highest modulus for phosphate glasses is for S-glass with 87 GP (DCL = 10).

For phosphate tribofilm glasses lowest modulus is 40 GPa (DCL = 1), and highest modulus is for steel with 220 GPa (DCL = 10). From curve slopes comparison we can conclude that phosphate tribochemical glasses have advantage over phosphate glasses of enhancing mechanical properties by factor of 3 ( Fig 1).

The MoDTC/ZDDP and ZDDP tribofilms possessed the same hardness of 10 GPa and the modulus of 215 GPa when the contact depth was greater than 20 to 30 nm [35-38]. Nascent aluminum was responsible for reacting with ZDDP and forming phosphide AlP and linkage isomer species of ZDDP [41-43].

The measured Young's modulus tribofilms were characterized by large smooth plateaus with value of 112 GPa and surrounding valleys with value of 54 GPa [44]. Indentation performed along a large antiwear pad gave an indentation modulus of 81 GPa [45].

## 4. Transformation of zinc phosphates in hard-core RMs after decomposition of zinc dialkyldithiophosphate (ZDDP)

The result of decomposition is a precipitate which contains 86% of zinc phosphate, 11% of zinc pyrophosphate, and 3% of sulfur compound and is in amorphous-colloidal state [47]. When such colloidal precipitates are placed in mineral oil in presence of surfactants, they are transformed into hard-core reverse micelles, RMs [27]. The term "hard- core reverse-micelles, RMs" is used to describe dispersions containing colloidal core, e.g., carbonate, borate, CuO, Ca-phosphate [27]. Hard-core reverse micelles of zinc metaphosphate, pyrophosphate and orthophosphate were prepared and tested on four-ball machine.

$$n\,Zn[O_2P(SR)_2]_2 \quad + \quad O_2\text{ (or ROOH)} \longrightarrow [Zn(PO_3)_2]_{colloidal} + [Zn_2P_2O_7]_{colloidal} + \text{ sulfur species}$$

The examination of colloidal precipitates from ZDDP decomposition and powder mixture of zinc metaphosphate and zinc pyrophosphate salts in ratio ( 9:1) in mineral oil in a 4-ball wear machine, provided comparable antiwear protection [47]. However, the antiwear effectiveness of phosphate powder in mineral oil in engine failed antiwear protection tests. The state of colloidal nanoparticles or amorphous zinc phosphates may be a critical parameter for effectiveness of antiwear performance.

Hard-core reverse micelles of zinc metaphosphate, pyrophosphate and orthophosphate were prepared under conditions such that zinc phosphates were formed by a chemical reaction ($ZnCl_2$ + with sodium meta-, ortho- and pyrophosphates) in presence of oleic acid/or calcium benzenesulfonate as the surfactant. Then colloidal solution was dispersed in hydrocarbon oil. The concentration of micellar zinc phosphate to oleic acid and mineral oil was 2:2:1,5 [27].

The physical structure of solid (powder) zinc phosphates and zinc might be a critical property in formation of stable composition in real engine oil. No antiwear benefit was observed for the phosphates powder addition to engine oil of zinc metaphosphate ($Zn(PO_3)_2$, pyrophosphate ($Zn_2P_2O_7$) and orthophosphate ($Zn_3(PO_4)_2$) [27, 47].

## 5. Conclusions

We have evaluated mechanical properties of the phosphate glasses, which formation is based on temperature-induced cross-linking changes, and have compared them with properties of phosphate tribofilm glasses. The phosphate tribofilm glasses formation is based on friction-induced changes in the coordination of the zinc atoms in the phosphates system, which results in cross-linking through the formation Zn-O bonds. We note, that the most important components in formation of chemically connected network of phosphate glasses and tribofilm glasses are cross-linking agents such as heavy metal. Adding the coordinating ions alters the pressure at which cross-linking occurs and increases the antiwear properties of the surface material significantly. Tribochemical phosphate glasses have advantage over phosphate glasses of enhancing mechanical properties by factor of 3 (see Fig 1). The degree of cross-linking during friction is provided by internal pressure of about 600 MPa and temperature close to 1000°C. These two factors lead phosphate tribofilm glasses to chemically advanced glass structures, which may enhance the wear inhibition.

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