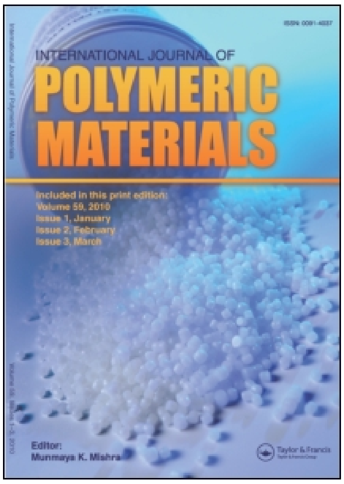

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Poly-Para-Phenylene-Copolymer (PPP): A High-Strength Polymer with Interesting Mechanical and Tribological Properties

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Poly-Para-Phenylene-Copolymer (PPP): A High-Strength Polymer with Interesting Mechanical and Tribological Properties

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This paper illustrates the high strength and modulus of a poly-para-phenylene-copolymer in comparison to other high-performance polymers. In particular, it outlines how its microhardness, fracture toughness, scratch resistance and specific wear rate against steel compare to corresponding values of polyether ether ketone.

Keywords mechanical properties, poly-para-phenylene-copolymer, scratch resistance, wear

INTRODUCTION

Poly-para-phenylene copolymer (PPP) (Teca-max SRP, Ensinger, Germany; or PrimoSpire self-reinforced polyphenylene SRP, Solvay, USA) is a new,

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The authors are grateful to the companies Ensinger GmbH, Germany, and Solvay Advanced Polymers, USA, who kindly supplied the PPP materials for investigation. Further thanks are due to the King Saud University, Saudi Arabia, for supporting this research collaboration. The help of the German Research Foundation (DFG) for enabling Prof. K. Friedrich to do a preliminary study on the scratch behavior of this material together with Prof. H.-J. Sue, Texas A&M University, USA, also highly esteemed.
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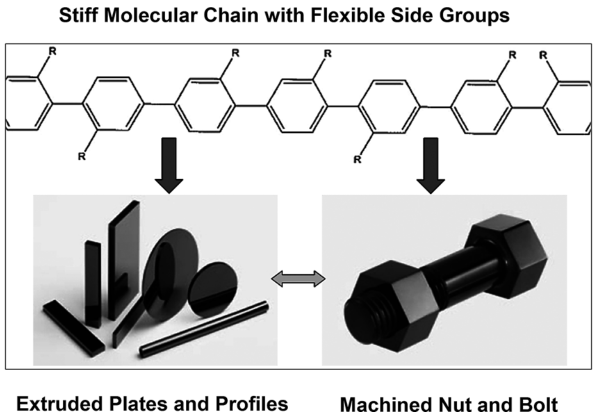


Figure 1: PPP-chain and products (*Source*: Ensinger).

ultra-high performance-thermoplastic material, which is based on very stiff poly (1,4-phenylene)-structured polymer chains [1–3]. At each phenylene ring, special substituents are attached, which allow it to become more flexible so it can be processed by extrusion or compression molding (Figure 1).

In this way, the stiff molecular backbone provides high strength and stiffness to the system, while the substituents lead to better processability. At present, this self-reinforcing polymer can be considered (at room temperature) as the stiffest, strongest and hardest polymer worldwide (i.e., without an additional type of reinforcement, such as short glass or carbon fibers). Preliminary studies have demonstrated a tensile strength of 207 MPa (i.e., higher than the yield strength of general purpose constructional steels, e.g., St33, DIN 17100 [4]) (Figure 2), a Young's modulus of 8300 MPa (much higher than polyetheretherketone PEEK, with 3650 MPa), a compressive strength of

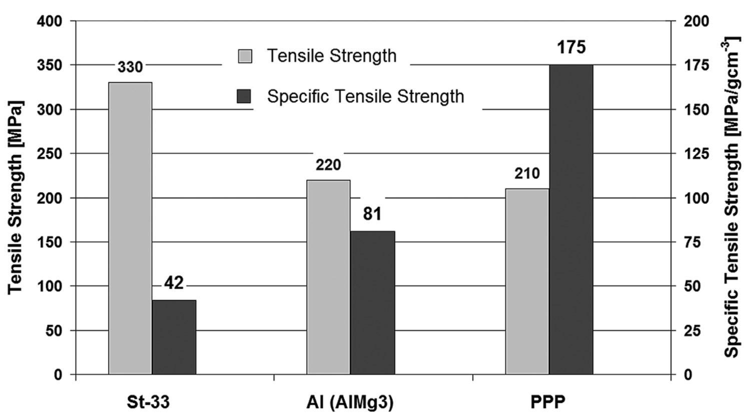


Figure 2: Specific strength (strength/density) of PPP vs. metals.

>620 MPa, and an impact toughness of 1200 kJ/m^2, all at a density of 1,21 g/cm^3. According to these values, it can be expected that this material also has exceptional properties under other loading conditions, of which the scratch and wear characteristics are of special importance for numerous applications, such as bearings, gears, sealings, flanges, valves, or thermal/electrical insulators. This can be of high interest for various users in the aerospace, automotive, medical and cryotechnology industries.

However, these tribological characteristics have not yet been studied and are, therefore, the focus of the present publication. For comprehensive understanding it is necessary to look at these properties from both a fundamental and an application-related point of view. In particular it is of interest how the temperature affects the mechanical performance of this polymer, and how the hardness, scratch resistance and specific wear rate are related to corresponding values of one of the best thermoplastic materials, polyetheretherketone.

MECHANICAL PROPERTIES OF PPP IN COMPARISON TO OTHER POLYMERS

According to some data published by the companies that produced this type of polymer (Ensinger, Germany; Solvay Advanced Polymers, USA), PPP possesses quite extraordinary tensile properties compared to other polymeric materials (Figure 3). Both modulus and strength are more than two times higher than corresponding values as measured for thermoplastic polyetheretherketone (PEEK) or thermosetting polyimide (PI). Looking at the flexural and compressive properties, the compressive strength value of PPP especially exceeds those of the three polymers tested in comparison (PEEK, polycarbonate PC, polyphenylenesulfide PPS) by a factor of 5 (Figure 4). With regard to the density and the thermal expansion coefficient, PPP

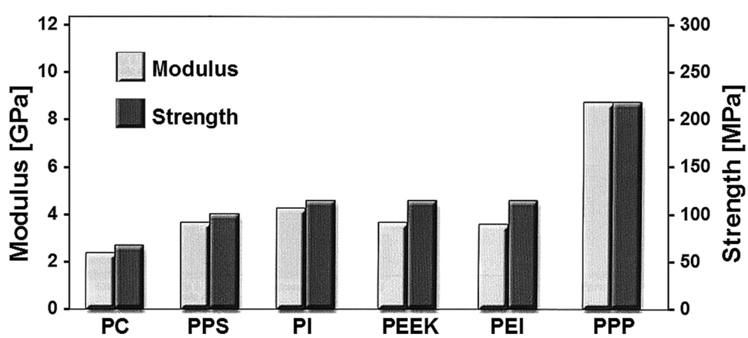


Figure 3: Modulus and strength ranking (*Source*: Solvay).

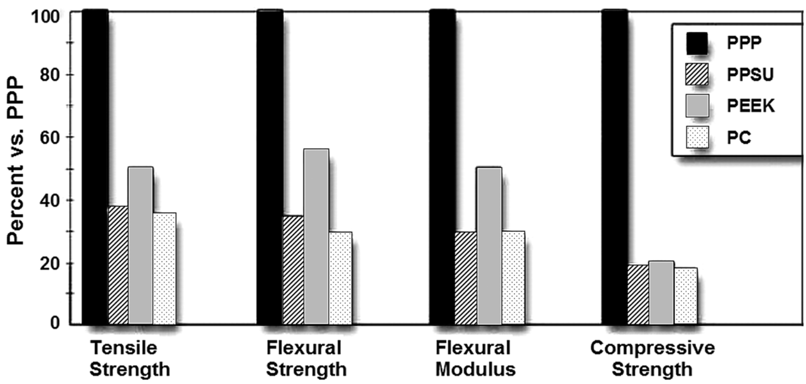


Figure 4: Ranking of mechanical properties (*Source*: Mississippi Polymer Techn., USA).

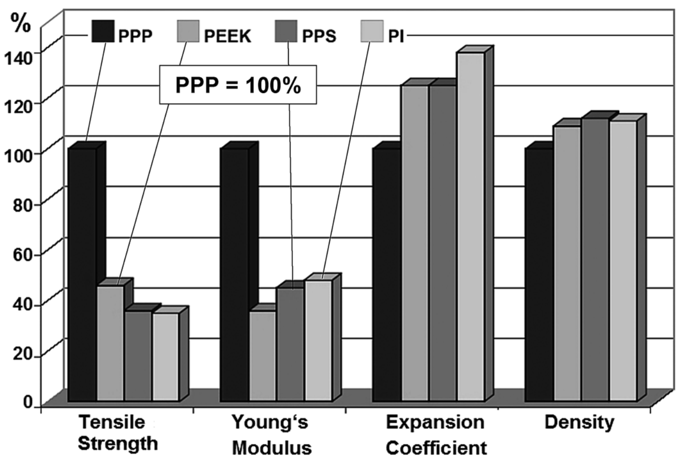


Figure 5: Different polymers and properties (*Source*: Ensinger).

exhibits slightly lower values than other polymers investigated in relation to it (Figure 5).

In general, one can conclude that PPP can be considered as a high performance polymer, which still offers (at room temperature) a great potential when other high performance thermoplastics or thermosets reach their mechanical limits.

EXPERIMENTAL TESTING PROCEDURES

Within this study, first the effects of temperature on certain properties of PPP were analyzed, using differential scanning calorimetry (DSC, Mettler

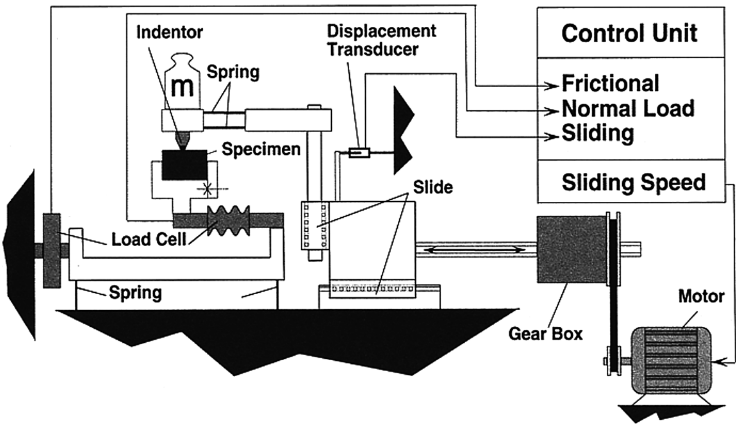


Figure 6: Scratch apparatus.

Toledo 821) and a dynamic mechanical thermal analyzer (DMTA, Gabo Eplexor 150 N). It was followed by studies of the universal hardness (Shimadzu DUH 202) and the fracture toughness, using single-edge notched tensile (SENT) test samples, machined out of extruded circular rods (diameter of 30 mm), as delivered by Ensinger GmbH. Finally, the scratch resistance was determined, using a diamond indenter under various loading conditions (Figure 6), and sliding wear tests against a classical ball bearing steel (German Standard 100 Cr6) were performed by both a block-on-ring and a pin-on-disc-configuration (Figure 7). The analysis of the scratch and wear mechanisms was carried out by the use of laser as well as light-scattering profilometry.

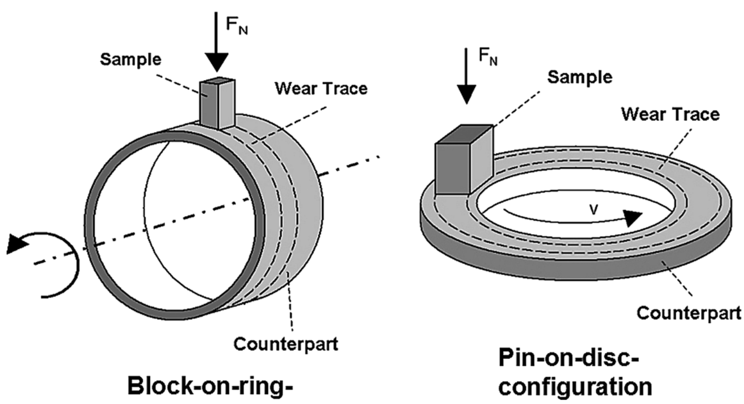


Figure 7: Wear test configurations.

RESULTS AND DISCUSSION

Thermal Behavior

Figure 8 illustrated the DSC scan of PPP. It can be seen that this material is amorphous since no crystal melting valley is visible on the heating-up run. However, a very distinct glass transition temperature signal occurs at 157°C, which can be considered as the upper temperature limit for the practical use of this material.

This can be better recognized from the DMTA-curves. The complex modulus E^* (Figure 9a), being at room temperature on the same level as reported before (ca. 8300 MPa), continuously decreased down to ca. 7000 MPa at 140°C, before it sharply dropped to zero in the range of the glass transition temperature. At the same time, the loss modules E^{**} (Figure 9b) increased sharply to a peak value at around 167°C.

Hardness and Fracture Toughness

The universal hardness HU of PPP in comparison to PEEK (Tape 450) can be calculated from the load-penetration depth-curves, as illustrated in Figure 10. The value measured for PPP (HU = 375 MPa) is almost 2 times higher than the hardness of PEEK 450 (HU = 191 MPa). From the curves, also a calculation of the elastic modulus can be derived by looking at the tangent to the load release branch of these curves [5]. This resulted in a value of 9370 MPa for PPP and a value of 4200 MPa for PEEK 450, confirming more or less the data from the literature and the DMTA-tests.

The critical stress intensity factor or fracture toughness K_{IC} was determined by sharp razor blade-introduced pre-cracks in the SEN-type tensile

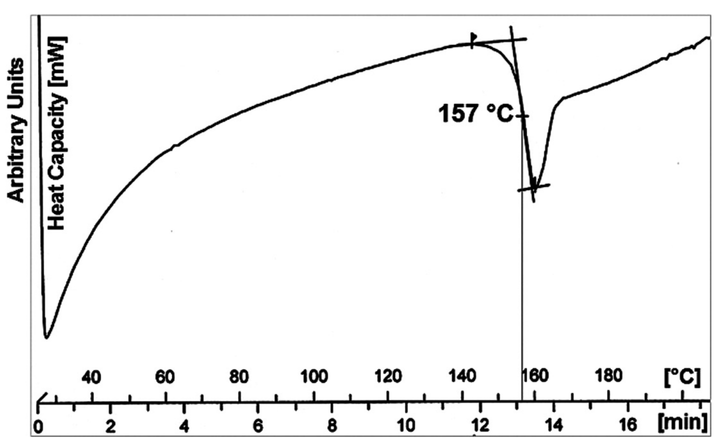
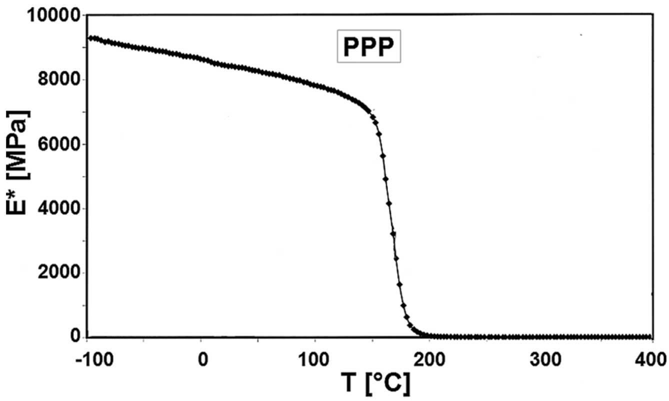
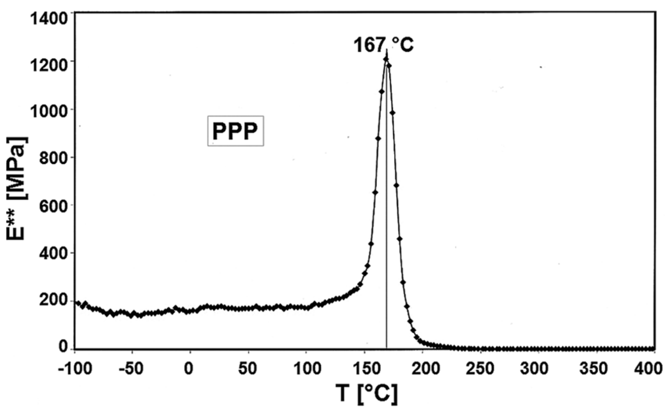


Figure 8: DSC-scan of PPP.



(a)



(b)

Figure 9: (a) DMTA-curve (complex modulus); (b) DMTA-curve/loss modulus.

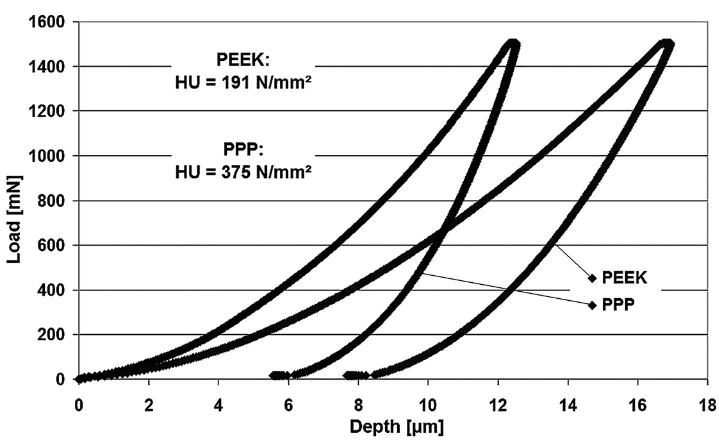


Figure 10: Hardness measurement.

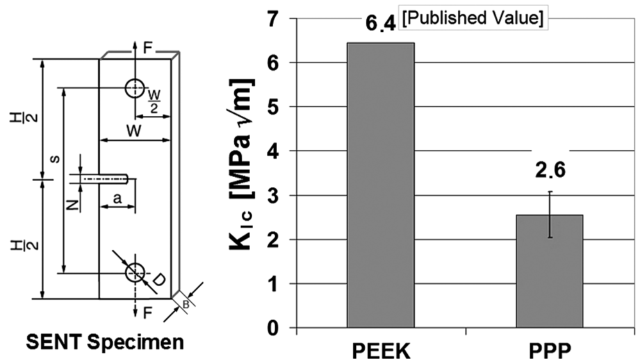


Figure 11: Evaluation of fracture toughness.

specimens (Figure 11). It turned out that the much harder PPP material performed in a more brittle way than the tough PEEK, which had a more than 2 times higher fracture toughness at room temperature.

Scratch Resistance and Specific Wear Rate

The relative resistance of the two different polymers under consideration (PPP vs. PEEK) can be estimated from the penetration scratch depth as a function of normal load, applied to the diamond scratch indenter (Figure 12). Especially at the higher load applied (1.5 N), PPP exhibits a resistance against scratch formation, being 3 times better than the PEEK material. This was evaluated from laser profilometer scans, as shown in Figure 13 for PPP.

An opposite tendency became obvious in the sliding wear tests against steel counterparts. Numerous studies on the wear of PEEK and its composites against 100 Cr6-steel confirmed that the specific wear rate of the neat polymer

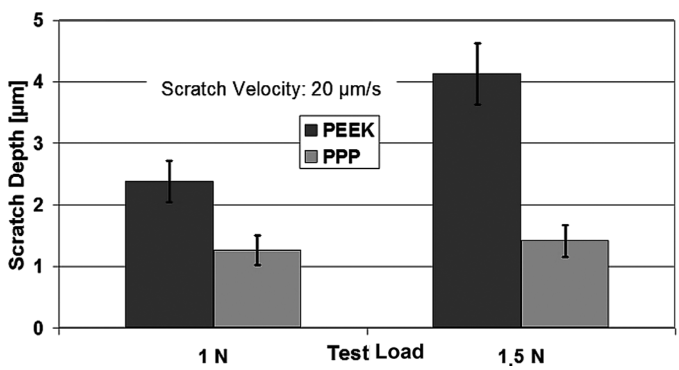


Figure 12: Scratch resistance tests.

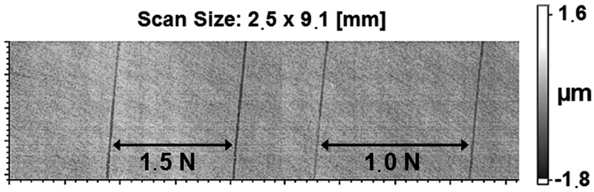


Figure 13: Laser profilometer scans.

varies between 9.3×10^{-6} and $7.6 \times 10^{-7}\,mm^3/Nm$, depending on the particular load collective (nominal pressure p and sliding speed v) applied [6]. The coefficient of friction measured under these conditions, varied around $\mu = 0.39$ [7]. A comparison of these values to the data measured for PPP under room temperature sliding conditions with a pin-on-disc-device clearly showed a higher friction and wear level of the PPP.

Figure 14 contains the course of the friction coefficient of PPP over a testing period of 20 h. After a relatively short running-in phase over 2 h, μ remained almost at a constant value of 0.47. This did not change very much when performing the tests at higher sliding velocities, as demonstrated in Figure 15. The corresponding wear rates are plotted in Figure 16, indicating clearly the wear rate dependence on the sliding speed.

The wear rate of PPP increased to a higher value (from $8 * 10^{-6}\,mm^3/Nm$ for 0.5–1 m/s to $22.7 * 10^{-6}\,mm^3/Nm$ for 2 m/s). The same trends were also found with the block-on-ring configuration (Figure 17). The discrepancies in the absolute values are simply a matter of the differences in the testing machines, various running-in conditions and the typical scatter known for wear studies in general.

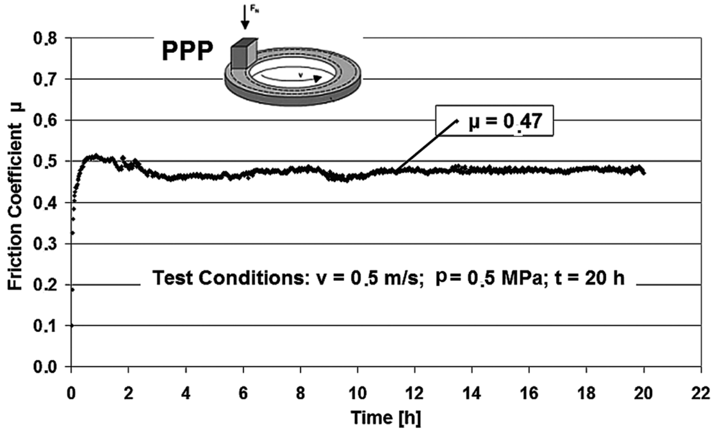


Figure 14: Course of the friction coefficient.

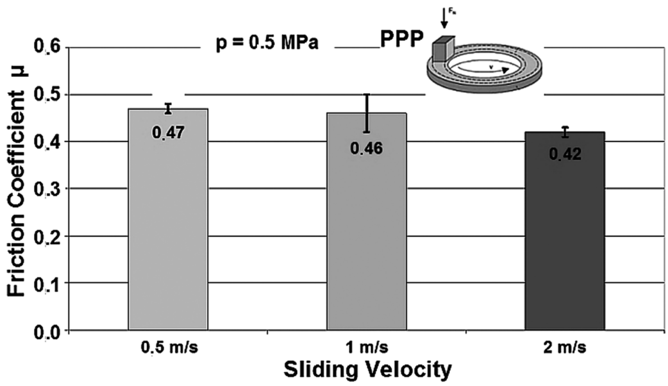


Figure 15: Friction coefficient (pin/disk).

Quite recently, a direct comparison of the PPP material with PEEK was carried out with a newly built wear testing machine at the company Nano-Profile [8]. In this case, the machine operates at a very low vibration, with high precision and over a wider load/velocity range, following the block-on-ring principle (Figure 18). Using a load collective of 1 m/s and 5 MPa, PEEK resulted in slightly better results than the PPP material (Figure 19). However, further studies have to be performed in order to understand these tendencies from a wear mechanisms' point of view.

Also the relationship between hardness and toughness with the scratch and wear performance must be carefully evaluated. Previous works of various authors [9,10] on different materials have shown that the usual tendency of an improvement in wear resistance with increasing hardness can be turned over into a negative tendency when all over sudden cracking mechanisms during wear dominate the process, especially when the material possesses a rather

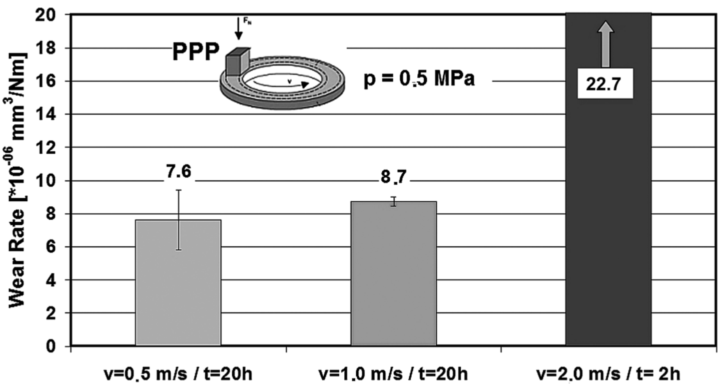


Figure 16: Wear rate (pin/disk).

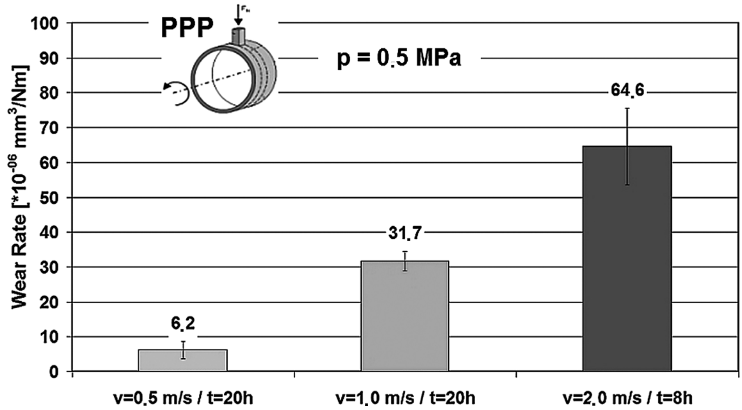


Figure 17: Wear rate (block/ring).

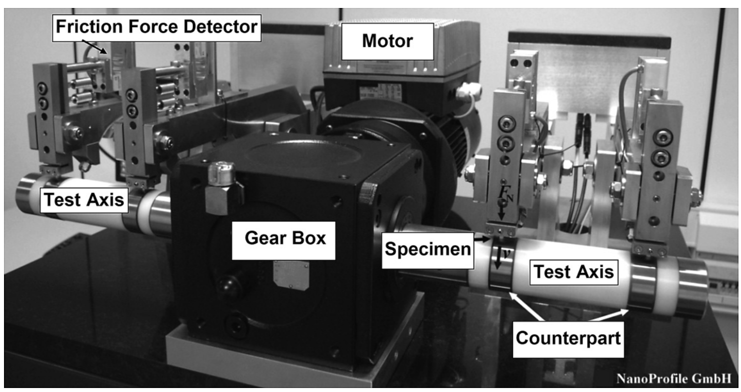


Figure 18: New block-on-ring testing machine at NanoProfile GmbH, Kaiserslautern, Germany.

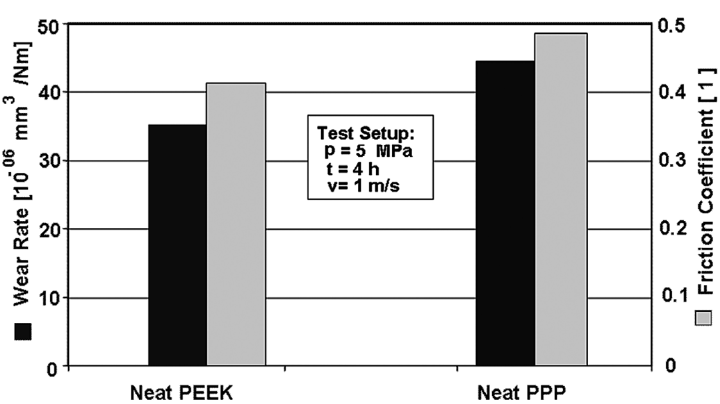


Figure 19: Comparison in friction and wear of PPP and PEEK.

low fracture energy. In this case, a relationship of the following form can describe the whole process:

$$w_s = \frac{\psi}{H^a} + \frac{\text{ø}H^b}{G_{IC}}$$

where w_s = specific wear rate, H = hardness, G_{IC} = fracture energy, ψ and ø are special co-efficients, and a, b and c are exponents of the order $\frac{1}{2}$ to 1 [11].

Whether or not such correlations also hold for PPP should be investigated in the near future.

CONCLUSIONS

In the present contribution, a new polymeric material, poly-para-phenylene-copolymer (PPP), was studied with regard to some thermal, mechanical and tribological properties. It turned out that this material has a high potential for many engineering applications, as long as the temperature range does not exceed 140°C. This is especially true for the mechanical loading under tension or compression, as long as the fracture toughness is not a very critical issue. The material possesses also a very high hardness and scratch resistance, which can be very helpful if good surface properties are requested for particular applications. However, the sliding wear resistance was not as good as the one measured for the neat PEEK, but it is assumed that this can be improved very much when incorporating special fillers into a PPP-matrix. This will be done in a future cooperation between the authors and one of the companies who supplied this material for investigation.

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