

Friction and wear properties of polyamides filled with molybdenum disulphide (MoS₂)

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Abstract

Polyamides (PAs) form a major class of tribo-polymers used in various types of friction and wear situations, especially because they exhibit advanced mechanical properties and abrasive wear resistance. In this paper, the influence of fillers like molybdenum disulphide (MoS₂) and nanoparticles in polyamides describing friction and wear behaviour was investigated. Reciprocating wear experiments were performed in polyamide 6 (PA6) and polyamide 6.6 (PA6.6) against low carbon steel counter plates using a medium scale flat on flat tribotester. The polymer test specimens were slid at a constant velocity of 10 mm/s and contact pressure of 10 MPa was included. The experimental results demonstrates that the friction coefficient of PA6 increase with increasing the temperature caused by frictional heating. PA6.6 composite filled with molybdenum disulphide (MoS₂) has lower coefficient of friction on comparing with PA6 due to the addition of nanoparticles. The PA6.6 sliding against steel is found to be more sensitive than PA6 to stick-slip motion, which complicates the wear mechanisms involved.

Keywords

Polyamide 6 (PA6), Polyamide 6.6 (PA6.6), carbon fiber, MoS₂, friction and wear.

1. Introduction

Thermoplastics have replaced metals in many light duty load bearing applications because of their lightweight, economic fabrication and good chemical resistance. The increase in use of polymers is due to the low coefficient of friction when compared with metals because of low interfacial adhesion energy [1]. The mechanical strength and wear resistance of polymers largely determine the suitability of these materials for applications like gears, bearings, cams, etc.[2]. Furthermore polymer gears and bearings can accommodate shock loading, shaft misalignment and bending better than the metal parts. Polyamide (PA) and polyacetal (POM) are the widely used thermoplastic polymers for engineering applications.

PA is one of the major engineering high performance plastics used in dry running applications for their good balance in properties. Thanks to their crystalline structure they show an excellent mechanical properties and chemical resistance. In addition, these materials have very good flame retardant property and can be extruded, thermoformed, or molded. Both polyamide 6 (PA6) and polyamide 6.6 (PA6.6) are widely used in many different markets and applications due to their good performance. They are by far the most used polyamide globally. In the recent years there is an increase in the usage of PA in food, medical, and chemical packaging applications [1]. Over 100 different formulations are available in the production of PA film, but PA6 and PA6.6 with melting point of 215, and 264°C, is commonly found polymer in food packaging applications [3]. Although they PA6 and PA6.6 exhibit similar properties some slight differences remain were PA6.6 has the following advantages on comparing with PA6 with better hydrolytic stability, lower cost, better long term heat ageing, the PA6.6 at 1.8 MPa is 80-90°C. PA6.6 is used in high temperature applications. It provides good surface appearance and good weld strength leading to burst pressure resistance. The water absorption properties of polymer are important because of influence on mechanical, electrical and tribological properties. PA6.6 has a lower absorption percentage of 8.5%, where PA6 which has 9.5%. The relatively high absorption percentage in PA6 is due to the high ratio of amide group to the CH₂ group were the amide group has a greater water absorbing property.

Several research has already been performed on the tribological behaviour of PA and it was fairly satisfactory even at dry sliding and lubrication was considered necessary only at high speeds [4]. However, this paper is focused on the comparison of the friction coefficient and the wear rate of PA6 and PA6.6 in the medium-scale testing with the goal to improve the fundamental insight into the tribology of these materials and to further extend the scientific perception of the influence of reinforced composites. In the last years various fillers have been used to develop polymers composites for high wear resistance, for example, short fibers reinforcements, such as carbon, glass and aramid fibers have been successfully used to improve the strength and therefore the load carrying capacity of polymers composites. In the other hand, with solid lubricants, such as polytetrafluoroethylene (PTFE), graphite and MoS₂ have proved to be generally helpful in reducing the coefficient of friction and consequently the wear rate. Nevertheless, all of those composites are used in polymer to increasingly applied as structural materials in the aerospace, automotive and chemical industries due to provide lower weight alternatives than metallic materials and a number of these applications are concentrated on tribological components, such as gears, cams, bearings and seals where the self-lubrication of polymers is of special advantages.

2. Materials and methods

Three different types of polymers with dimension of 30x30x30 mm³ have been used in the current investigation, commercially available (Zell Metal, Austria).

PA6 (Zellamid 202XN) is reinforced by nanoparticles. PA6.6 (Zellamid 250) is one of the hardest and most rigid types of extruded nylon. And the last PA6.6 (Zellamid 250MO) filled with Molybdenum disulphide (MoS₂) having improved strength, rigidity and friction ratio (Table 1). Main characteristics of all the three polymers are high resistance to react with fuels, oil, greases, most organic solvents and alkalis. However, Zellamid 250 and Zellamid 250MO has low moisture absorption rate which ensures better dimensional stability. Before the test the samples are machined by milling, and the arithmetic mean roughness was found to be 3.5 μm .

Table 1. Properties of the polyamide PA6 and PA6.6

Property	Unit	Zellamid 202 XN	Zellamid 250	Zellamid 250 MO
Density	g/cm^3	1.15	1.15	1.15
Tensile strength at break	MPa	93	80	80
Elongation at break	%	5	50	50
Modulus of elasticity in tension	MPa	4200	3200	3200
Hardness Shore, Scale D		80	80	80
Moisture absorption	%	3	2.8	–
HDT	$^{\circ}\text{C}$	168	100	–
Melting Point Method A	$^{\circ}\text{C}$	215	255	265

S235JR low carbon steel (1.0037, EN10025) plates were used as counter material for all experiments, with dimensions of 100mm x 200mm x 20mm. The chemical composition of the counter plates are summarized in Table 2. The surface finishing of counter plates was obtained by means of grinding. The surface roughness of the counter plates was measured before and after the tests using a Hommel Tester T1000 according to DIN EN ISO 4287 standard with an assessment length $l_t = 4.0$ mm and cut off $\lambda_c = 0.80$ mm. The resulting R_a roughness values before tests were found between 0.6 and 0.7 μm .

Table 2. Chemical composition and properties of S235JR carbon steel.

Material	C[%]	Si[%]	Mn[%]	P[%]	S[%]	Cr[%]	Ni[%]
S235JR	0.22	0.35	1.10	0.05	0.05	0.3	0.3

3. Test-setup

The medium-scale tests were performed on a flat on flat setup a schematic view of the test rig is shown in the figure 1, the adaptability of testing of the

convenience to handle the system. Beside, the results can be extrapolated to large scale thus making the test more economical. The test bench is built on a fatigue rated load-frame with 200 kN capacity. Two steel counter-faces (2) are mounted (bolt connection) on a central sliding block (1). This central sliding block is connected to the actuator of the load frame. The sliding block moves in the vertical direction and slides against the two specimens (5) placed in holders (4). The maximum normal load which can be applied on the friction specimens is 225 kN. The test material (5) and the holders (4) are held in (vertical) position by the reaction fork (3). Wear of the friction material is compensated by horizontal movement of the holders (4) with respect to the reaction fork (3). The reaction fork is constructed in such fashion that it can also hold the test medium. The characteristics of the test rig and the test parameters are mentioned in Table 3.

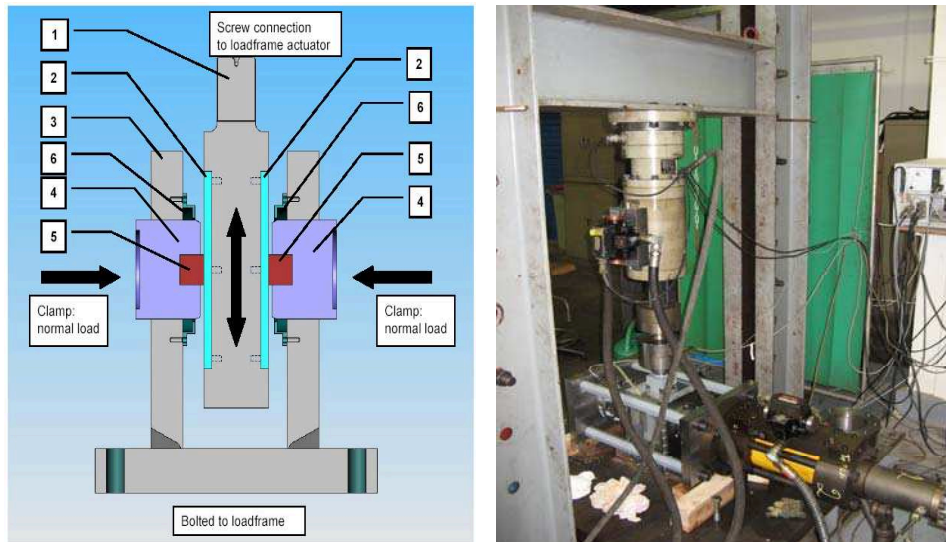


Figure 1. Medium-scale flat (MSF) tribotester

Table 3. Test parameters

Parameters	Units	Limits
Size of test material	[mm]	30 x 30 x 30
Size of counter (steel) material	[mm]	80 x 200 x 19
Maximum stroke	[mm]	100
Maximum normal load	[kN]	225
Maximum friction force	[kN]	200
Maximum frequency at maximum stroke	[Hz]	1

4. Test Procedure

Initially the moisture absorbed by the test specimen from the environment is removed by drying the specimen in an oven for 24 hours at a temperature of 70°C. The specimen was cooled in a controlled atmosphere before measuring the weight and the thickness. Flat polymer materials are slid against flat counter plates to simulate flat on flat condition. Visual inspections were made to ensure the parallelism between the counter plate and the specimen. The used sliding stroke was 10 mm, furthermore the running-in was done for 72 hours with a constant load and velocity at 9000N, 10mm/s respectively, 10 mm was the sliding stroke, Cooling is done in order to study the change in temperature during the initial period of contact which is normally high. After cooling for 4 hours the test was performed for two hours with the same load and velocity. A total of seven loops were done to identify the accuracy level of the test.

5. Calculation of the friction coefficient

For all the measured signals the scale factors and offsets were applied. The total friction force (F_{FR}) is measured by the force transducer. The coefficient of friction (μ) is calculated from the measured friction force (F_{FR}) and the normal force (F_N) according to equation 1, where in the factor of two is used because the friction force is the aggregate of the two friction specimens.

$$\mu = \frac{F_{FR}}{2 \cdot F_N} \quad (1)$$

The values of friction force in the beginning of sliding will be considered for calculating the static coefficient of friction (μ_{stat}). The dynamic coefficient is the average the second half of the stroke (μ_{dyn}).

6. Results

Parameters like friction force, temperature, and displacement due to wear of material were recorded and the results are summed up for analysis.

The friction coefficient during the 72 hours test is shown in Figure 2(a). Considering the difference between the static and the dynamic friction all the three materials follow the same pattern having larger values for static friction comparing the dynamic friction Figure 2(b) shows the friction coefficient from 76 to 78 hours. The main purpose of running-in for 72 hours is to have a proper surface orientation on polymers to have an error free result. Moreover, the specimen is allowed to cool for four hours from 72 hours until 76 hours. A difference in the range between the running-in period and the test period is

observed. During the running-in period the friction force between a thermoplastic and the steel surface aligns.

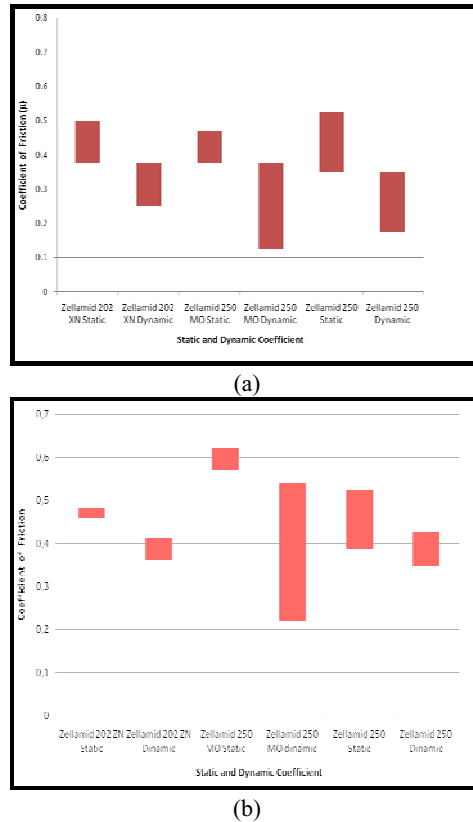
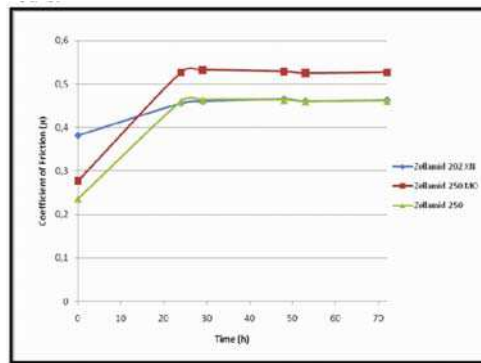


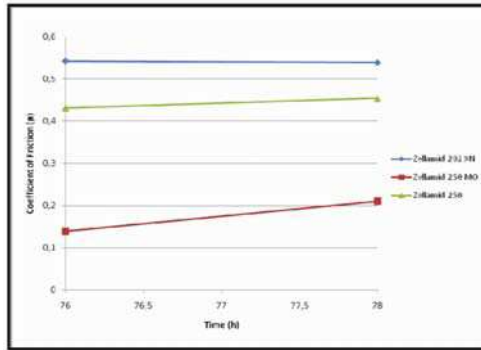
Figure 2. Illustrates the range of friction coefficient between all three materials (a) 0 – 72 hours (b) 76 – 78 hours.

The figure 3(a) and (b) shows the friction curves for the running in period for all three test material from 0 to 72 hours. The curve for friction coefficient was made as function of sliding distance (h) where a constant load and sliding velocity of 9000N, 10 mm/s and sliding stroke 10 mm is maintained. Both the static and dynamic friction shows similar behaviour with respect to the sliding distance or sliding time (h). It worth to note that the tendency of the friction coefficient curves is similar in both, forward and reverse directions considering the absolute values. Figure 3(a) shows the friction curves for all three materials during the running in period where the friction coefficient increases dramatically during the initial stage from 0 to 20 hours and then follows a steady pattern until 72 hours. The dynamic friction coefficients among the three materials during two hours from 76 to 78 hours is shown in figure 3 (b) and it clear the friction coefficient is relatively lower in Zellamid 250MO when compared with the other two materials. Both materials Zellamid 250 and Zellamid 202 XN have a similar

trend in the friction curves. Moreover, Zellamid 202 XN produces has high friction coefficient on comparing with other two polymers.



(a)



(b)

Figure 3. Coefficient of friction Vs. Displacement during running-in: steel – PA 6.6 (Zellamid 250 MO); s= 64 mm; P= 11-10 MPa; velocity= 10 mm/s for (a) Running –in 0-72 hrs (b) Test period 76-78 hrs

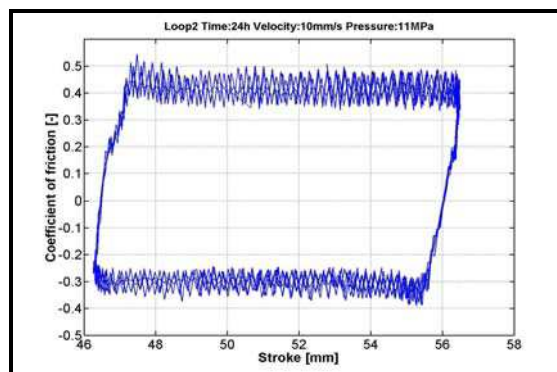
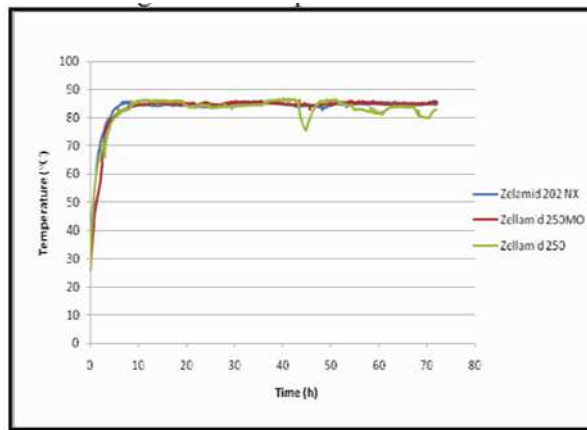


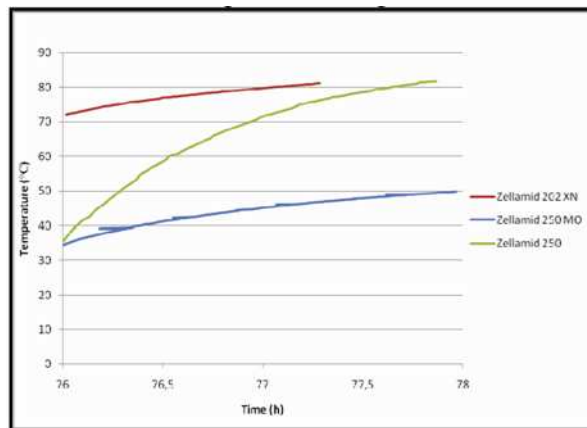
Figure 4. Friction Force vs. Tangential displacement after every standstill, steel-PA6 (Zellamid 202XN), P=11MPa, v=10mm/s, cycle 1. Show stick-slip effect during the initial period from 46.6 mm to 47.05 mm the stroke.

7. Influence of temperature

It is evident from Figure 5 (a) and (b) that for all the three materials the temperature increases to a specific limit initially and reaches a steady state where the temperature remains constant. During the running-in phase, the temperature of the specimens increases above 80°C as shown in the Figure 5 (a). The temperature of contacts surface increases with sliding distance due to the frictional heat developed during sliding. Figure 5(b) shows the increase in temperature with respect to the sliding distance from 76 to 78 hours and in all the three materials it was found to be linear. The friction and wear behaviours might also depend on the temperature rise of apparatus used. Among all three samples Zellamid 250 MO has the lowest effect of temperature during the test.



(a)

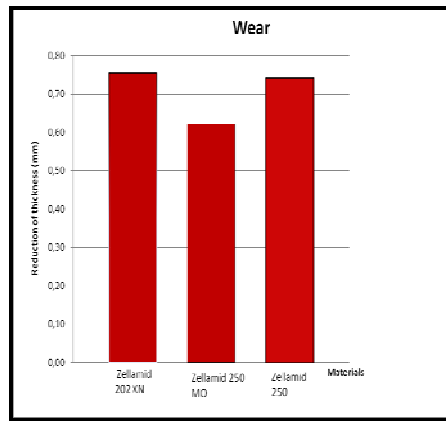


(b)

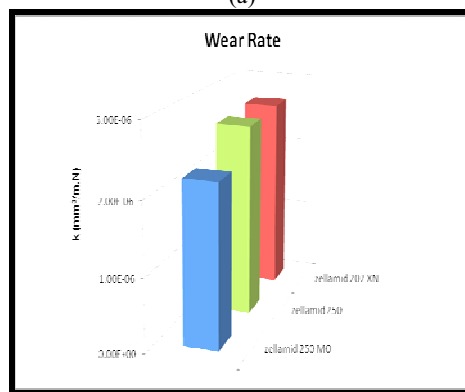
Figure 5. Temperature of Zellamid 202XN, Zellamid 250 MO and Zellamid 250, (a) From 0-72 hours, (b) From hour 76-78.

8. Wear rate of the polymers used in testing

The total thickness reduction of the three different polymers blocks during the tests at a constant load and velocity is shown in the Figure 6. The total thickness reduction results from the combined action of the following mechanisms: elastic and plastic deformation, thermal expansion and wear (material loss). In order to distinguish real wear (material loss) from deformation, the weight loss of the test material was also measured and thus the wear was calculated. One sample was tested to compare the results for analysing the accuracy level of the experiment. It is clearly seen in Figure 6 Zellamid 250 and Zellamid 202 XN has the highest wear when compared with Zellamid 250 MO. The actual wear (material loss) of the plastic blocks is caused by abrasion, which could be expected for such rough counter plates. No material transfers due to adhesion of the plastic material to the steel counter surfaces were observed. And wear debris on the sides of the wear track gives possible evidence for abrasion.



(a)



(a)

Figure 6. (a) Illustrates the wear rate of the three materials (Zellamid 250 XN, Zellamid 250 MO, Zellamid 250 from 76 to 78 hours), (b) Wear (material loss).

9. Discussion

The main objective of the current research is to investigate in the friction and wear behavior of the PA6 and PA6.6 which could be used in bearing applications. The friction and wear behaviour of polymeric matrix materials can be improved by having a lower surface tension and high stiffness which is obtained quite successfully by using reinforced or filled with nanoparticles to the polymers. Internal lubricants such as PTFE or graphite are frequently incorporated to the polymers to reduce adhesion. Additives like short aramids, carbon, or glass fibers are used to increase stiffness, strength, impact resistance, thermal conductivity, and creep resistance of the polymers. With a blend of high-performance polymer matrix, internal lubricants and fibrous reinforcement, excellent friction and wear properties can be achieved in composites. In our case additives like nanoparticles and molybdenum is added and the effect of these additives is clearly seen from the results were the friction behaviour of the material changes corresponding to the additives.

Previous research has been conducted with different speeds and it was found that friction coefficient at of nylon reaches a maximum of 1.0-2.0 only higher speeds[5]. The friction coefficient increases rapidly until 20 hours, on comparing the increase in temperature were the relationship between temperature and the friction coefficient is linearly dependent on each other. Two mechanisms controls the friction force F between a thermoplastic and steel: adhesion and deformation of the plastic [6] were adhesion occurs as product of the real contact area and the shear strength of the plastic material. An increase in glass transition temperature (which equals 40-50 °C for PA 6) leads to a gradual decrease in the elasticity modulus E which dominates the deformation mechanism. The difference in the friction curves during the forward and the reverse stroke is possibly due to the asperity interactions were breaking and regeneration of micro junctions. The asperities are broken down during the forward traverse causing a increased value in friction coefficient relative to the reverse stroke were new asperities are formed during the reverse stroke. Moreover, this is explained as the result of frictional heating which increases the temperature of the contact surface, leading to relaxation of polymer molecule chains [7]. Some variations are observed in the friction coefficient are possibly due the critical surface energy of the polymer

In others investigations it was found that for line and point contacts, the flash temperatures at running-in are at maximum due to the high contact pressure in the initial stage [8] this is due to the intensity of heat to a confined area is relatively small on comparing with flat on flat test configuration, this phenomenon is eliminated. It was evident that temperature played a vital role in the material behaviour, for example in all three material from 76 to 78 hours showed a behavior correlating the raise in temperature were the friction coefficient decreases with the increase in temperature. However, considering all the three polymers, the highest temperature was observed in Zellamid 202 XN (PA) which is due to the material property with respect to the strength by

softening were the mobility of the chains increases as they become less rigid. Nevertheless, this higher mobility also makes it easier to remove wear debris from the bulk specimen. Melting can also occur because of the higher temperatures and plastic deformation is more at higher loads. Both effects contribute to a severe wear regime for PA6.

For apparent contact pressure which is sufficiently low to neglect the interaction of the individual contact spots between rough surfaces, the real contact area or the indentation of the hard asperities into the softer material is proportional to the normal load for both elastic and plastic deformation. Such a situation results in a friction coefficient independent of the normal load where the softer material has a constant shear. In our case the load is of the range in between large scale and the medium scale testing causing plastic deformation as a dominant mechanism. As PA6 is a thermoplastic, it deforms more easily at interactions with the harder steel roughness asperities of the mating surface when its temperature is higher. Consequently, at higher temperatures the roughness asperities of the steel counter surface plough through the PA, rather than normal separation of the rubbing surfaces due to the forced tangential motion from the inclinations of roughness peaks over one another (asperity interlocking). The normal vibration caused by asperity interlocking lead to a reduction in the friction force at higher velocities. Figure 5 shows that the mean coefficient of friction during stick-slip is lower than during smooth sliding. During stick-slip serious vibrations of the entire test rig were observed. From the literature, it is known that both normal and tangential vibrations lead to a reduction in the friction force [9, 10]. Therefore, it is well known that for abrasive wear processes the surface roughness especially that of the hardest surface, is extremely important. The higher the surface roughness of the hard surface, the higher the ploughing and abrasive wear. The friction coefficients of thermoplastic polymers PA6.6, PA6 first decrease with increasing surface roughness of the steel counter plate and reach minimum values at R_a about 0.2-0.5 μm . With further increasing roughness the friction coefficient increases. The explanation for this behavior in the literature [11] is that, for small values of the surface roughness, adhesion forces are the dominating factor, whereas for higher surface roughness, abrasive processes prevail. The literature supports the finding that abrasive wear of polymers increases considerably with growing surface roughness of the steel mating plate [8].

The influence of particles size plays an important role of the wear resistance was due to either mechanical (the enhanced modulus and hardness practically) or chemical (the improved bonding between transfer films and metallic counterparts) reasons similar effects were observed by Wang et al [12] where the effect of Molybdenum disulphide (MO) additives and nanoparticles in PA 6.6 was investigated recently where PA with MO particles do not have a favorable result but when blended with carbon fibers shows significant improvement in wear resistance of PA 6.6 and higher coefficient of friction. The research work done by Pettarin et al [13] also showed same results of having increased wear

resistance by adding molybdenum disulphide is contributed through the heating effects. It was also observed in our case that the Zellamid 250 MO has the lowest temperature relative to the other two materials where MoS₂ helps in the dissipation of generated heat during friction and thus having high wear resistance.

10. Conclusions

Systematic flat on flat wear experiments at medium-scale on three polyamides: Zellamid 202XN, Zellamid 250 MO and Zellamid 250, in reciprocating sliding contact with low carbon steel counter plates under normal load of 9000N and sliding velocity of 10 mm/s revealed that tribological properties are affected by chemical composition, mechanical properties of the thermoplastic, service temperature as well as reinforcement by means of nanoparticles. PA 6.6 (Zellamid 250) sliding against steel is sensitive to stick-slip motion and favorable behaviour in friction and wear was observed in the PA6.6 with Molybdenum disulphide additives. The highest friction coefficient and wear level was encountered with Zellamid 250 the PA6 without any additives. The molybdenum disulphide additives influence the material to have high wear resistance and low coefficient of friction.

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References

1. Czichos, H., et al., Advances in tribology: the materials point of view. *Wear*, 1995. 190(2): p. 155-161.
2. Thorp, J.M., friction of some commercial polymer-based bearing materials against steel. *Tribology International*, 1982. 15(2): p. 69-74.
3. Soto-Valdez, H. and J.W. Gramshaw, Cyclopentanone and cyclopentanone derivatives as degradation products of polyamide 6,6. *Journal of Materials Science Letters*, 2000. 19(10): p. 823-825.
4. Srinath, G. and R. Gnanamoorthy, Effect of short fibre reinforcement on the friction and wear behaviour of Nylon 66. *Applied Composite Materials*, 2005. 12(6): p. 369-383.

5. Watanabe, M., M. Karasawa, and Matsubar.K, frictional properties of nylon. *Wear*, 1968. 12(3): p. 185-&.
6. Y.Yamaguchi, *Tribology of plastics materials Tribology series Vol. 16.* 1990: Elseiver.
7. Unal, H. and A. Mimaroglu, Friction and wear behaviour of unfilled engineering thermoplastics. *Materials & Design*, 2003. 24(3): p. 183-187.
8. Van de Velde, F. and P. De Baets, The friction and wear behaviour of polyamide 6 sliding against steel at low velocity under very high contact pressures. *Wear*, 1997. 209(1-2): p. 106-114.
9. Tolstoi, D.M., Significance of the normal degree of freedom and natural normal vibrations in contact friction. *Wear*. 10(3): p. 199-213.
10. Lenkiewicz, W., The sliding friction process--effect of external vibrations. *Wear*, 1969. 13(2): p. 99-108.
11. Lancaster, J.K., Dry bearings: a survey of materials and factors affecting their performance. *Tribology*, 1973. 6(6): p. 219-251.
12. Wang, J., et al., Investigation of the influence of MoS₂ filler on the tribological properties of carbon fiber reinforced nylon 1010 composites. *Wear*. 255(1-6): p. 774-779.
13. Pettarin, V., et al., Changes in tribological performance of high molecular weight high density polyethylene induced by the addition of molybdenum disulphide particles. *Wear*. 269(1-2): p. 31-45.