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Tribological Analysis of the Nano-modified Industrial Polymer

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Abstract

The aim of this paper is research of positive influence of the commercially available nano-additive on tribological properties of the essential polymer for the industry. The nano-filler amount was chosen equal to commonly needed for amending of other paramount properties of the polymer. The tribological behavior of polymer nanocomposite was investigated during the rubbing against low alloyed steel in oilless contact. The composites consist of Ultramid which was modified by 1, 3 and 5 wt.% of nanoclay Cloisite. Samples were tested on T-05 block-on-ring tribometer and observed with SEM and Laser Confocal Microscope LEXT OLS 3000. There were observed a positive and pronounced effect of nano-additive on temperature regulation in contact zone, investigated and analyzed other aspects of tribological behavior of a polymer/steel contact joints.

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1. Introduction

Recently the application of polymers has increased generally in technology and also as materials for dubbing components in machines and devices. The development of new technologies creates new requirements for bearings and wear resistant materials that cannot be satisfied by traditional metallic materials. A low coefficient of friction in the complete absence of any lubricant, an absence of corrosion of parts which can be affected by salted water or humid climate, - these and many others aspects are of considerable interest to engineers. As well the low cost of

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materials and manufacturability of large amount of components have the great importance for the industries.

The wear and friction of non-metallic solids have some significant differences to that of metals: the wear mechanisms involved and the level of friction or wear which occurs [1]. The most important factors which determining level of wear due to sliding friction and magnitude of the coefficient of sliding friction are hardness and surface roughness of the paired materials, contact pressure, traversed distance, temperature of the sliding surfaces and lubrication. The difference of application of polymers in frictional contacts in comparison to metals and ceramic materials relates mainly to the chemical and physical structures as well as to the surface and bulk properties. Polymers show very low surface free energy and also have visco-elastic properties. It effects in drastic tribological differences when we consider adhesive and mechanical components of friction force. The steel-on-polymer frictional tribosystem is the most popular and also practically confirmed as the best tribological combination [2-4]. Relatively low friction coefficient and often sufficiently high wear resistance can be achieved in these systems by proper selection of the polymer and steel to be use.

However, only a few polymers do have valuable tribological properties and most researches are directed towards this relatively limited number of polymers [1].

Compared with other polymers, polyamides are widely used as bearing, guide, gear and other sliding parts, have high strength and stiffness, excellent chemical resistance and superior antifriction and wear resistance. Ultramid offers high thermal stability of parts, dynamic strength, impact resistance and long-term performance. It has great potential for the economically optimized production of structural components and modules. Ultramid has proved to be superior to aluminum in withstanding wear stresses of this nature which play a significant role in water pumps for example. Fans and automobile spoilers for example are exposed to this type of stress which is caused by granular solids entrained in streams of air or liquid. The advantageous elastic behavior of Ultramid results in high resistance in this case.

In spite of outstanding properties the polymer composite materials are not finally investigated, and there are still staying some of old but very important aspects which need our further researches. There are required improvements of tribological properties of materials, which lead to life prolongation of polymeric materials and critical details and as the result increase reliability of constructions. And one of the most perspective methods is to fill it by nanoparticles.

The reported data evidence a strong influence of nano-additives on the structure and properties of polymers. This is especially pronounced with nanoclays [5-7]. One of the main reasons for this is strong adsorptive interaction of macromolecules with rather developed filler surface, and also polymer transition to some particular conditions with constricted molecular mobility. The increased cohesive strength of the polymer binder can result in the improved tribological properties of the composites such as the abrasion resistance and resistance to fatigue wear.

At strong adsorptive interaction of nanofillers and macromolecules the molecular mobility becomes abruptly frozen in the polymer amorphous phase. The functional groups in macromolecules become blocked by the interaction with the filler surface [6]. As the result, the obstacles are created that prevent from adhesive interaction with the counterface, and the adhesion component of friction force decreases. The presence of nanoparticles within a friction contact may influence the processes of the mass transfer, the accumulation of static electricity, the heat transfer on individual sites of contacting surfaces, the creation of real contact areas, etc. Thus, effects of nanofillers on the tribological properties of polymers can alter both bulk and surface properties of the materials.

The general idea behind the addition of the nano-scale filler is to create a synergy between the various constituents. The properties of polymer nanocomposites rely on a range of variables, particularly the matrix material, which can exhibit nano-scale dimensions, loading, degree of dispersion, size, shape and orientation of the nano-scale second phase and interaction between the matrix and the additive.

An advantage of using nanoparticles compare to macro- or micro-fillers as reinforcement is that their size is smaller than the critical crack length that typically initiates failures in composites. Nanoparticles can act as voids and provide improved toughness and strength to the composites. They can also significantly affect glass transition temperature. Typically this occurs because nanoparticles influence the mobility of the polymer chains due to bonding between the nanoparticles and the polymer and bridging of the polymer chains between the nanoparticles. Higher the interaction between matrix and nanoparticles, more it affects glass transition temperature, as it will increase.

Nomenclature

F_0	static friction force
F_s	steady friction force
P	force of normal pressure
μ_0	static coefficient of friction
μ_s	steady coefficient of friction

2. Experiment

This paper investigates the tribological behavior of Ultramid which was modified by 1, 3 and 5 wt.% of nanoclay Cloisite during rubbing against low alloyed steel in oilless contact. Samples were prepared by extrusion mixing process. Tribological experiments were carried out on a block-on-ring T-05 tribometer with the following experimental parameters: block width 4 mm; sliding radius 17.5 mm. Test time was chosen 120 min., that allow us to investigate parameters of running-in and regular steady regime of work. Normal load was 20N. Sliding speed variants were chosen in accordance to the exploitation regimes of a real friction joints and correspond to 0.43, 0.55, 0.70, 0.80 and 0.92 m/s. The friction force, displacement and the temperature in contact zone for each test were continuously recorded during the test time. Worn surfaces were observed and wear tracks measured by a Laser Confocal Microscope LEXT OLS 3000 and SEM.

3. Results and discussion

The following factors affect considerably the friction force: the contact load, sliding velocity, and temperature. The effects are not independent, for example, depending on the contact load and velocity the contact temperature may vary considerably changing the friction mode. On the present stage of research the load variation factor is excluded.

Theoretically, the friction force should not depend on the sliding velocity [5]. For polymers, however, this statement is only true if the temperature within the contact area grows but negligibly. Usually there is a complex dependence of the friction coefficient on the velocity explained by variations in the relaxation properties and physicochemical activity of macromolecules. On the Fig.1 we can analyze the practically resulting friction force performance of various composites at three time points.

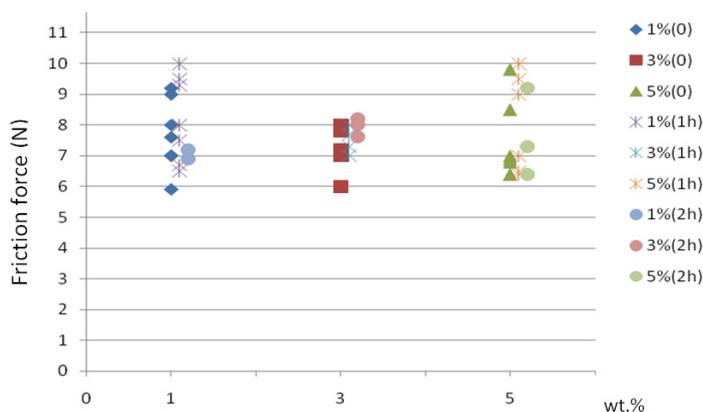


Fig.1. Time performance of the friction force of various composites at the beginning (0), middle (1 hour) and at the end of the test (2 hours), with filler content labeled.

According to sources [8, 9] the main mechanisms of wear for polymers are adhesion, abrasion, and fatigue. Abrasive wear is caused by hard asperities on the counterface and hard particles that move over the polymer surface. This mode of wear occurs when the roughness is the determinative parameter in friction.

The adhesive mode of wear occurs in the sliding of a polymer over unlike surface, e.g. metal, when the strength of the adhesive bonds formed between the contacting materials can exceed the cohesive strength of the polymer. As a result, some part of the material is transferred onto the counterface and forms a transfer film; another part of the worn material is removed from the friction zone as the wear debris.

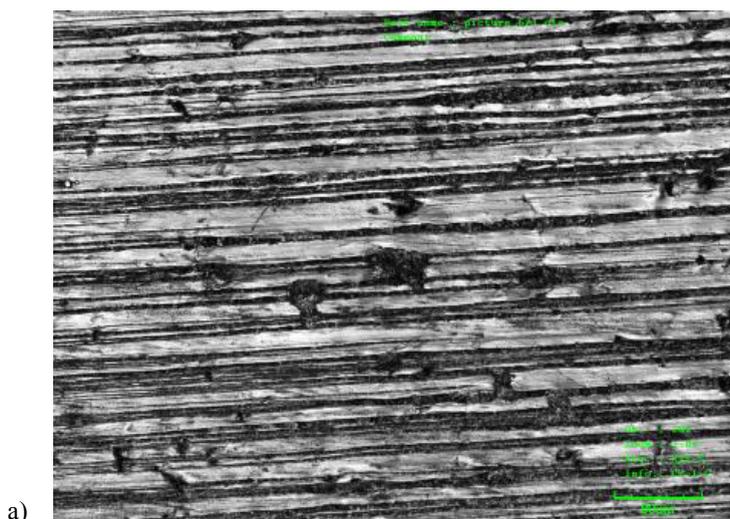
The fatigue wear of polymers is caused by the crack propagation at the repeated deformation of the material at friction. Fatigue results in the pitting, crack generation. The wear debris are formed as a result of the growth and intersection of the small cracks on the polymer surface which are perpendicular to the sliding direction. The fatigue wear occurs after prolonged friction that may be important in the absence of adhesive wear when the counterface is smooth.

In general, three stages of wear can be distinguished: running-in, steady regime and catastrophic wear [10]. As applied to a metal/polymer friction system, the first stage implies the generation of a transfer film on the metal counterface. For most metal/polymer systems the tribological characteristics much depend on the properties of the transfer film, i.e. its nature, strength of bonding to the metal surface, the part of the counterface area covered with the transfer film, the severity of adhesive interaction on the polymer/transfer film interface. This has been supported experimentally and reported by several authors [9, 11, 12]. As polymers adhere to hard surfaces through absorption [13] it can be assumed that the adhesion component of the friction force depends on the absorptivity of macromolecules. Immobilization of their functional groups and constraining the molecular mobility must affect strongly the tribological behavior of the polymer.

The friction of polymers over metals is greatly affected by tribochemical reactions occurring in the contact zone [14]. The tribochemical transformations in macromolecules follow the free-radical mechanism consisting of three main stages: initiation of macromolecules; growth of chains and their termination.

The direction and kinetics of chemical processes in polymers depend not only on the chemical structure of macromolecules but also on the arrangement of molecules, perfection and size of crystallites, the degree of molecular orientation, and molecular mobility. The structural heterogeneity in polymers leads to non-uniform distribution of additives and reagents in their bulk. In the partially crystalline polymers the low-molecular weight substances (oxygen, products of oxidation, inhibitors, plasticizers, dyes, fillers, etc.) tend to concentrate in the amorphous regions of the polymer; most reactive fragments of macromolecules are also localized there. The local concentrations of reagents may differ much from the average concentrations; consequently, the local rates of tribochemical reactions must be different from the average rates. Thus, the introduction of additives into the polymer that alters its physical structure unavoidably affects its tribological properties.

Visual analysis of the worn surfaces (Fig. 2) confirms the numerical results of the graph (on Fig. 1).



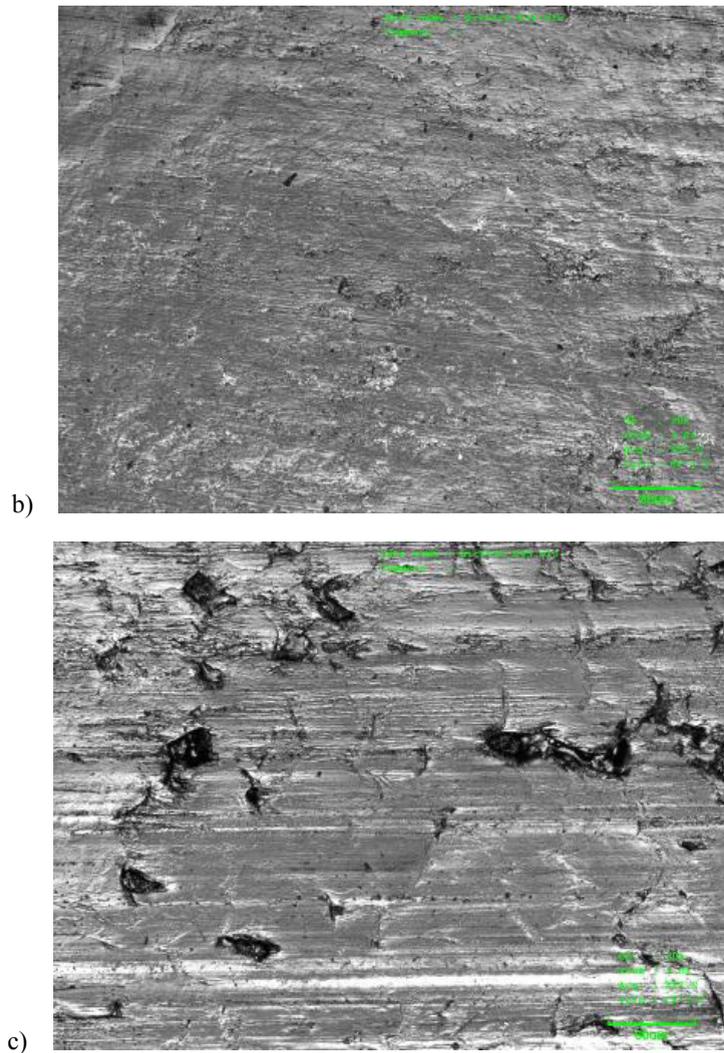


Fig. 2. Worn surfaces in 480 times multiplication , applied velocity 0.92 m/s, content: a) 1wt.%; b) 3wt.%; c) 5wt.% of nano-particles.

The worn surfaces of samples with 3wt.% of nanoclay is smoother, this is also proved by the roughness data analysis. This fact give us opportunity to make the suggestion that Cloisite content equal to 3wt.% is an optimal amount of nano-additive.

The mechanisms of energy dissipation at deformation can be described next way: when a polymer with visco-elastic behavior slides over a hard rough surface energy dissipation is caused by the high hysteresis losses. This deformation component is known as friction due to the elastic hysteresis [5]. Elastic hysteresis occurs when a varying force repeatedly deforms an elastic material. The produced deformation doesn't disappear completely when the force is removed, and this results in energy loss on repeated deformations. Additives strengthen the polymer by reducing elasticity. That is good until the defined point, the overstepping of which we can observe in the case of the composite with the 5wt.% of nanoclay (Fig.2c). As the result the wear level significantly increased. The energy may also be carried away with elastic waves generated at the interface and outgoing to the infinity, owing to the nucleation and development of microcracks in the material [5,15] – the fatigue wear development.

Without an exception in all applied tests friction contacts were accompanied by adhesion and further it results in micro-cutting, that is, an additional work was done increasing the friction force.

The mechanical component results from the resistance of the softer material to “ploughing” by

asperities of the harder one. The adhesion component comes from adhesive bonds formed between the surfaces in the friction contact. It is believed that for polymers the adhesion (molecular) component exceeds much the mechanical one [16], due to transfer films generated on the metal counterface. Special consideration is given to transfer films as the key factor which determines the tribological behavior of polymer materials [8,9].

At the Fig. 3 are shown examples of friction force dependence on time for the samples with the same nanofiller content but tested with different speed conditions. They were observed by continuously recording of characteristics during the test time.

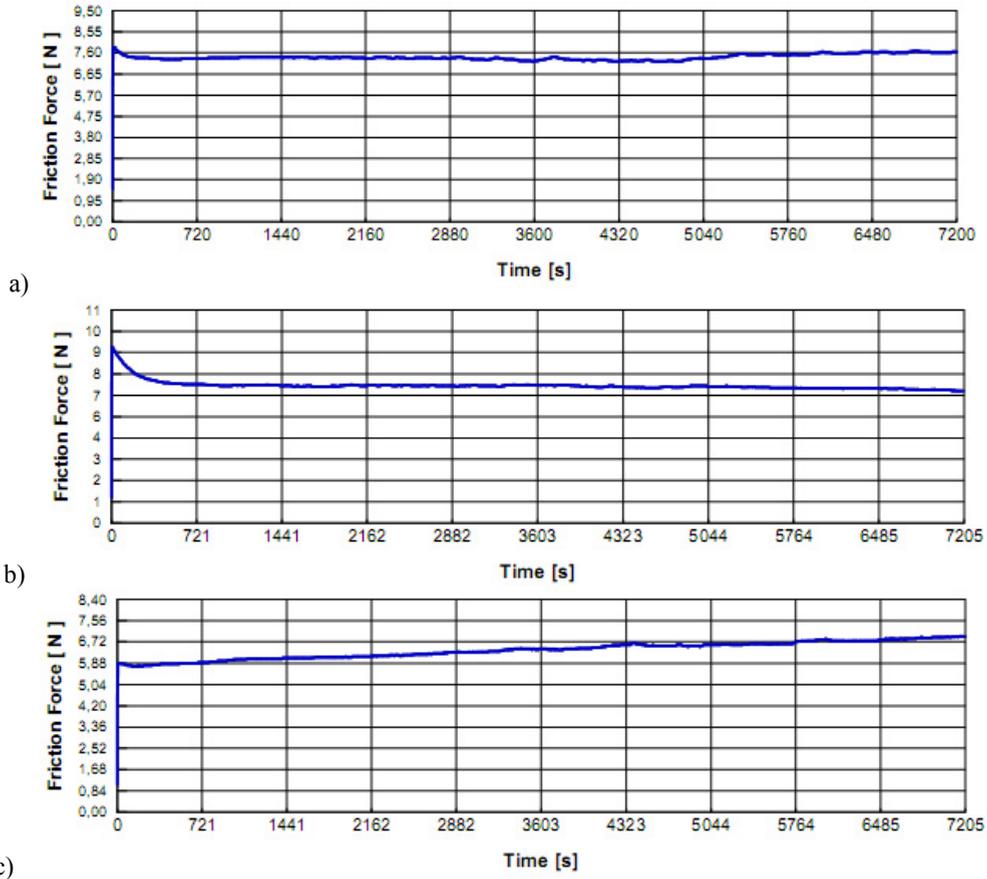


Fig. 3. The example of the friction force behavior of composite material in dependence of time at sliding velocity a)0.43, b) 0.7, c) 0.92 m/s.

It is known that the force required for starting moving is needed for breaking of the adhesive bonds between the counterbody surfaces. There are existing two cases [17]:

- In the first case the friction force grows until the F_0 (the static friction force) and then decrease to the quasi-steady magnitude F_s . It means that the static coefficient of friction:

$$\mu_0 = \frac{F_0}{P} \tag{1}$$

where P – the force of normal pressure,
is higher than the quasi-steady coefficient of friction:

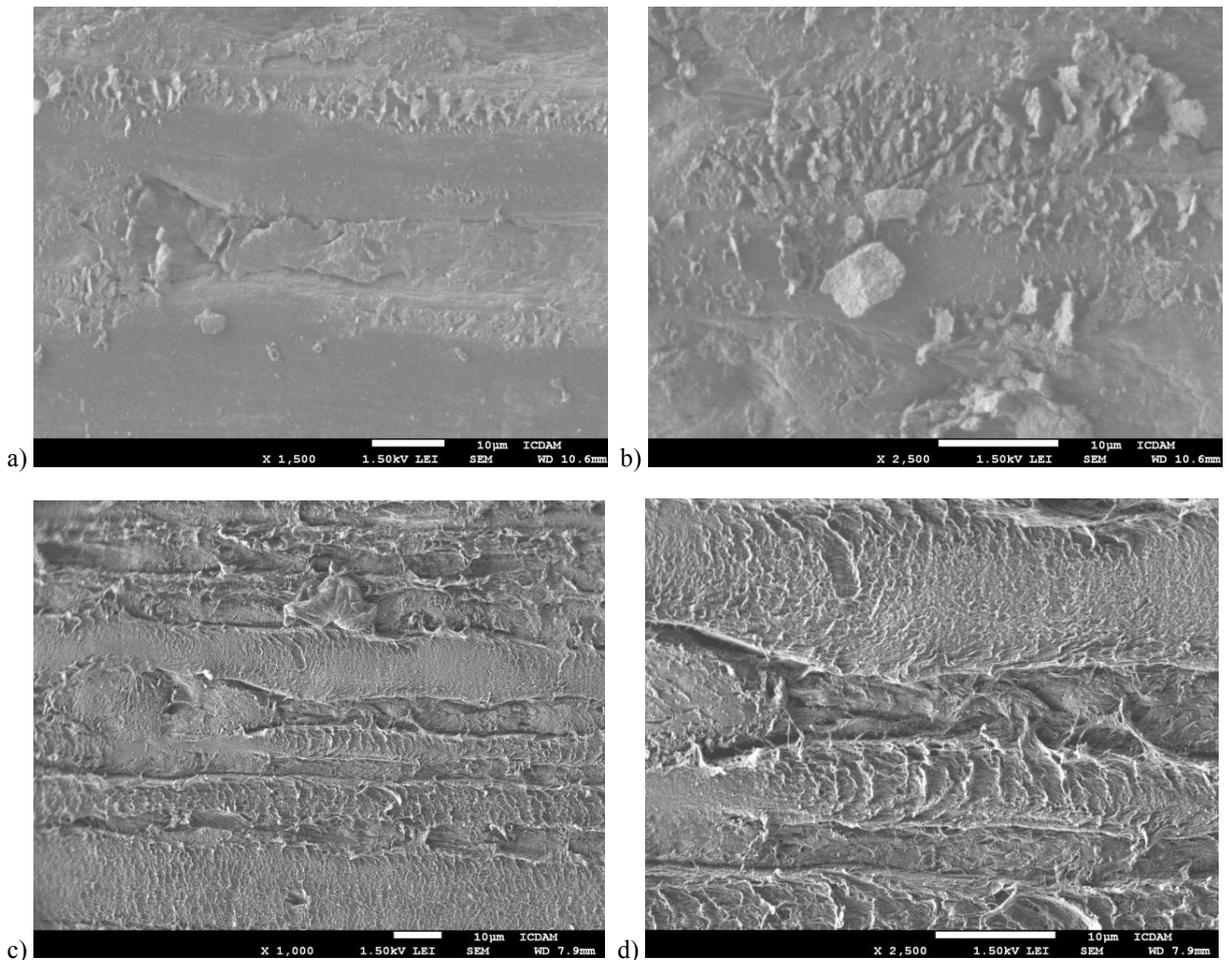
$$\mu_s = \frac{F_s}{P} \quad (2)$$

Thus, at the beginning of sliding the friction coefficient grows to the μ_0 value, which corresponds to strength of adhesive bonds. After the break of the initial bonds appears equilibrium of the creating and bursting bonds. So that the friction coefficient decreases to μ_s .

- In the second case the velocity of adhesive bonds creation is close to the sliding velocity, thus:

$$\mu_0 \approx \mu_s \quad (3)$$

At the graph which corresponds to the lowest sliding velocity we can observe realization of the second case. The frictional behavior which describe us the graph for the middle sliding velocity corresponds to the first case. At the higher velocity appends the influence of growing heat in contact zone. Increase of the temperature rise the mechanical component of the friction force in the issue of the resistance of the softer material to “ploughing” not only by asperities of the harder counterbody but the particles of the started destruction process. It is difficult to separate the effects of the velocity and temperature on friction.



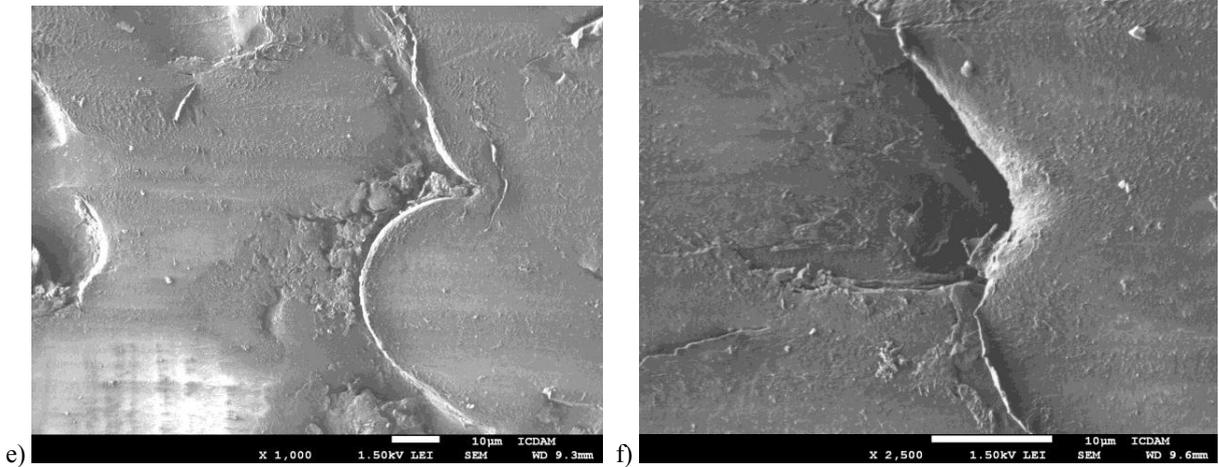


Fig.4. Contact zone of the samples with 5wt.% after 2 hours of friction under load of 20N and speed (a,b)0.43, (c,d) 0.70 and (e,f) 0.92 m/s.

At the pictures made with SEM (Fig.4) are represented sample with the same filler content, tested with the different velocities. Their comparison helps us to review and analyze processes and material behavior in the contact zone.

Polymers as visco-elastic materials are very sensitive to frictional heating. It is commonly known that heat generation at friction results from the deformation of the material on real contact spots [5]. Another source of heat can be attributed to the formation and rupture of adhesive bonds. These processes are most probably energetically non-equivalent and the energy difference may cause the generation or absorption of heat.

The noticeable result of nanofiller influence, which we could see directly from the graphs of continuously recorded characteristics, is the reduction of the temperature in the contact zone. The time and the velocity variations were specially chosen for indication of this effect. At the graph Fig.5 we can see the comparison of the temperatures at the most indicative points: at the beginning, middle and at the end of the experiments.

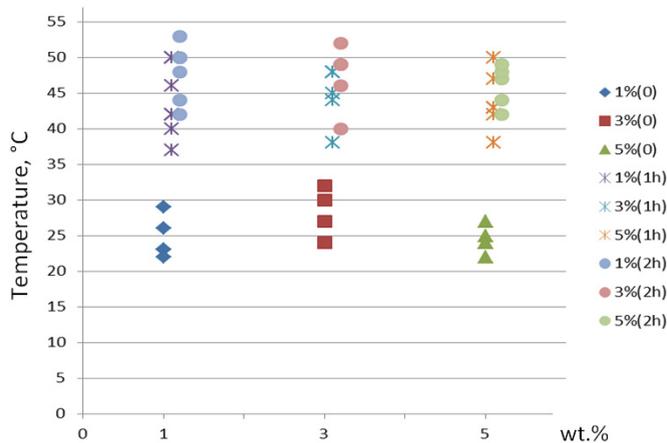


Fig. 5. The time performance of the temperature in the contact zone of various composites, with filler content labeled.

The laboratory environment at the test time caused the moderately higher initial temperatures of the samples with 3wt.%. However, the middle and the final temperatures in contact zones for them are lower than for the samples with 1 wt.%. Thus we can see that the addition of the filler significantly reduce the heating of polymer samples during the tests which can be taken in correspondence to the work process of tribological joints of the real mechanisms. Higher content, like 5 wt.%, could has more pronounced effect but as we can see from comparison on

Fig. 2, the fatigue mode of wear appears, and Fig. 4(e,f) proves this, as the result the wear level significantly increases according to Fig.1. Also it should be noticed that the filler increases the dissipation of heat. Samples with 3 wt.% of nano-additive shown lower heating in the contact zone in the friction process than the samples with 1 wt.% in spite of the higher initial temperatures.

4. Conclusion

This work contains the investigation of influence on the tribological properties of commercially available nano-additive in the amount commonly needed for improvement of other paramount properties of the essential polymer for the industry.

As compare to metals thermal conductivity has the main influence on operational conditions of the polymer composites as well as on its thermal decomposition. At present moment for the evolution of composite materials the questions about mechanism of improvement and the influence of nanofillers on the tribological properties and taking those parameters under control become paramount.

Thus, the study of additional range of properties of already well pronounced in tribological sense structures is an important and actual scientific problem.

There was observed a positive and pronounced effect of nano-additive on temperature regulation in contact zone and thus on tribological behavior of a polymer/steel contact joints. The analysis of erased surfaces, roughness, friction force and the temperature changes in contact zone were carried out. And according to observed results it is also should be considered that the „break“-value [18] of nano-Cloisite containment for the Ultramid is 3wt. %. Higher concentration of the nanoclay filler further improves the thermal properties of the composites, but it also changes the other aspects of the wear mechanism, which should be taken into account.

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