Tribological properties investigation of the thermoplastic elastomers surface with the AFM lateral forces mode

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Abstract. The series of new thermoplastic elastomer films based on copoly(urethane-imide)s (coPUI)s and nanocomposites containing from 1 to 10 wt. % carbon nanofillers of different morphology (single-walled carbon nanotubes, carbon nanofibers, and graphene) as well as WS_2 and WSe_2 nanoparticles, were prepared and investigated by atomic force microscopy in contact mode. The friction coefficient (C_{fr}) on the films surfaces under conditions of true slip was determined both in one scan field and with multiple scans (200-400) in one place. The measurements were carried out at room temperature and at a heating up to 120°C. It is shown that at heating up to 75-85°C, the friction coefficient of some coPUI decreases significantly. The same effect can be achieved also after 100 scans during multi-scan testing at 20°C.

1. Introduction

The surface properties of the polymer films play a decisive role in their applications especially if they used as coatings [1]. Atomic force microscopy (AFM) is an indispensable technique to study the various surface phenomena [1-4]. AFM allows not only evaluating the roughness of the surface, but also recognizing the different localized phases and revealing the distribution of friction forces over the surface in the micro- and nanoscale [5-7].

The aim of this work was to study the tribological characteristics of a series of novel multiblock (segmented) copolymers, containing rigid imide blocks and flexible blocks of polyurethanes – copoly(urethane-imide)s (coPUI)s and their nanocomposites, in microscale using AFM in contact mode. The study included the friction coefficient measurement at the temperature range from 20 to 120 °C and multipass friction force determination over 400 scanning areas.

2. Experimental details

For synthesis of new multiblock coPUIs, the 1,3-bis (3',4-dicarboxy-phenoxy) benzene (dianhydride R) and 4,4'-bis-(4'-aminophenoxy)diphenylsulfone (diamine SOD-*pair*) with various ester fragments, as well as an aliphatic copolyester (Alt), secondarily terminated with 2,4-tolylene diisocyanate, were used [8]. The chemical structures of the coPUIs are presented in Figures 1 and 2.

The nanocomposite films based on them containing from 1 to 10 wt. % carbon nanofillers of different morphology – single-walled carbon nanotubes (SWCNT), carbon nanofibers (VGCF), graphene, and WS_2 and WSe_2 nanoparticles were prepared. The studied samples are listed in Table 1.
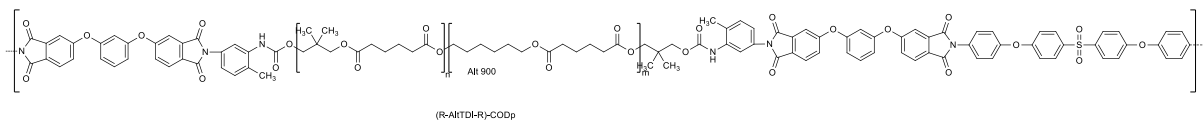
Figure 1. Chemical structure of coPUI (R-AltTDI-R)SOD*p* matrix.
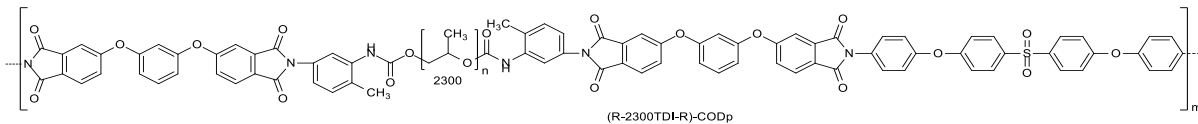
Figure 2. Chemical structure of coPUI (R-2300TDI-R)SOD*p* matrix.

The microscale roughness, friction coefficient, and friction force of the samples were investigated using AFM device NT-206 (produced by MTM Belarus). The surface morphology was studied using standard CSC38 silicon probe with the radius of tip curvature less than 10 nm and stiffness of cantilever 0.08 N/m produced by MikroMash (Estonia). The surface roughness was investigated in scanning areas 2x2, 5x5, and 10x10 μm^2 (Table 2).

The force and friction coefficient were measured using 20x20 μm^2 scanning areas with silicon probe NSC11 of V-shaped type with stiffness 3 N/m at the moving speed 1.55 $\mu m/s$. The tip radius was specially blunted by pre-scanning to curvature 100 nm. Such preparation prevents the probe from further blunting and keeps the contact condition stable. C_{fr} is calculated from a ratio of the friction force between two bodies and the normal force pressing them together; their measurement is described in [2]. To measure the friction force, the AFM probe scans the surface in so-called two pass method. During the first pass, the probe goes forward along the surface. On the second pass, it moves according to the first line, which suits the relief. During the forward and backward ways the friction forces from the surface influence on the tip, which causes the torsion of the cantilever besides its deflection in the normal direction (angle α in Figure 3). The angle of this twist depends on the value of the friction force. To calculate the effect of frictional forces more precisely, the angle of twist, when the probe is moved in the forward and backward directions, is divided in half.

Table 1. Samples of coPUIs and nanocomposites based on them investigated in this work

| Matrix	Matrix symbol	Additive	Additive content, %	Composite symbol
(R-2300TDI-R)SOD*p*	50	-	-	50
		VGCF (nanofiber)	1	50 + 1% VGCF
		SWCNT (single-walled carbon nanotubes)	1	50 + 1% SWCNT
		Graphene	1	50 + 1% Graphene
		WS$_2$	3	50 + 3% WS$_2$
		WSe$_2$	1	50 + 1% WSe$_2$
(R-AltTDI-R)SOD*p*	45	-	-	45
		WS$_2$	10	45 + 10% WS$_2$
		WSe$_2$	10	45 + 10% WSe$_2$
		VGCF (nanofiber)	1	45 + 1% VGCF
		SWCNT (single-walled carbon nanotubes)	1	45+ 1% SWCNT
		Graphene	10	45 + 10% Graphene

Table 2. Roughness of the studied samples measured using AFM

Composite symbol	Side	Roughness, nm					
		Scanning area 10x10 μm^2		Scanning area 8x8 μm^2		Scanning area 5x5 μm^2	
		Ra	Rq	Ra	Rq	Ra	Rq
50 + 1% Graphene	1	–	–	21.98	33.54	3.23	5.09
	2	–	–	20.51	26.04	18.14	23.09
50 + 1% SWCNT	1	–	–	43.73	56.40	21.69	26.11
	2	–	–	44.62	53.19	21.42	26.46
50 + 1% VGCF	1	6.21	12.91	–	–	3.40	4.40
	2	47.74	62.14	–	–	26.69	34.54
45 + 1% VGCF	1	8.16	11.84	–	–	7.54	10.6
	2	22.82	28.71	–	–	19.39	24.21
45 + 10% Graphene	1	–	–	87.61	110.2	148.5	177.0
	2	–	–	46.93	58.46	25.94	32.99
45+ 1% SWCNT	1	–	–	21.24	26.29	13.81	16.95
	2	–	–	76.13	95.96	72.40	83.28
45	1	4.53	5.71	–	–	2.69	3.36
	2	–	–	3.948	4.48	–	–

C_{fr} was determined in several regimes: for one scan field for one line in the forward and backward directions, and for the multiple scans (200-400) in one place. The measurements were carried out both at room temperature and at 120°C. The heating was carried out directly during the scanning process using a thermoplatform placed on the AFM table. The thermoplatform is equipped with heaters and a feedback system with sensors, which allows controlling the heating and automatic reducing the voltage, if necessary, to maintain the fixed temperature.

3. Results and discussion
Typical images of the coPUI matrices and nanocomposite surface are presented in Figure 4. According to AFM images, the differences in morphology of the films surface between two sides of the films can be clearly seen. It can be concluded that their structure and morphology are extremely sensitive to the substrate surface. Hence, the effect of additives influence on the films structure is much greater than confirmed by AFM images.
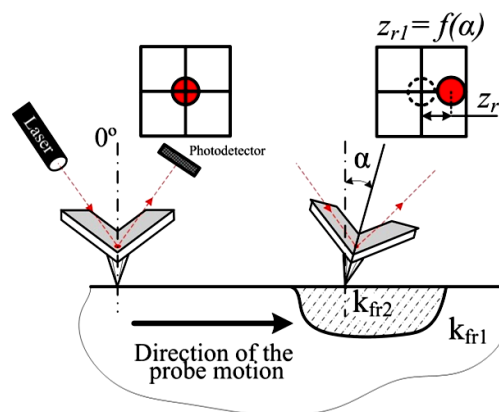

Figure 3. The scheme of cantilever twist under the action of friction forces.
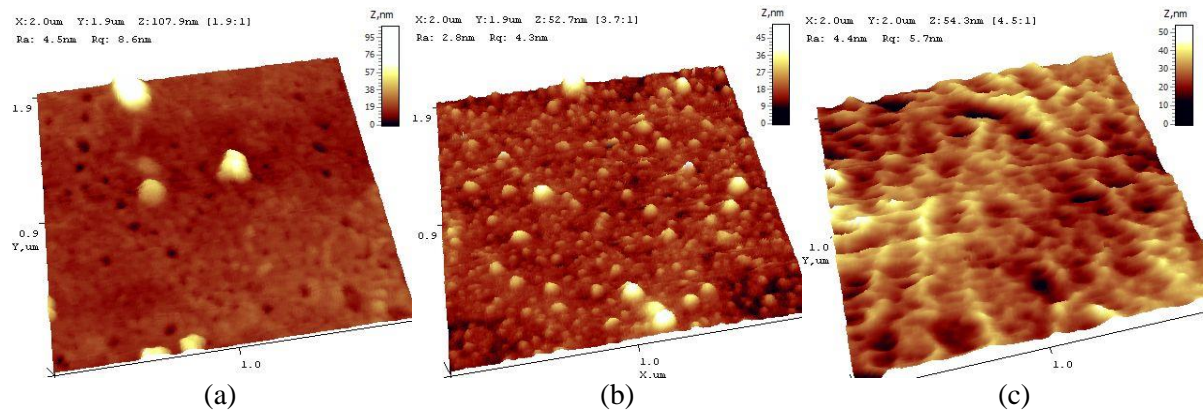
Figure 4. Three-dimentional images: (a) neat (R-AltTDI-R)SOD*p* matrix; (b) R-AltTDI-R SOD*p* matrix with WS_2 nanoparticles; (c) coPUI (R-2300TDI-R)SOD*p* matrix with WS_2 nanoparticles. Scanned area 2x2 μm^2.

(a)

(b)
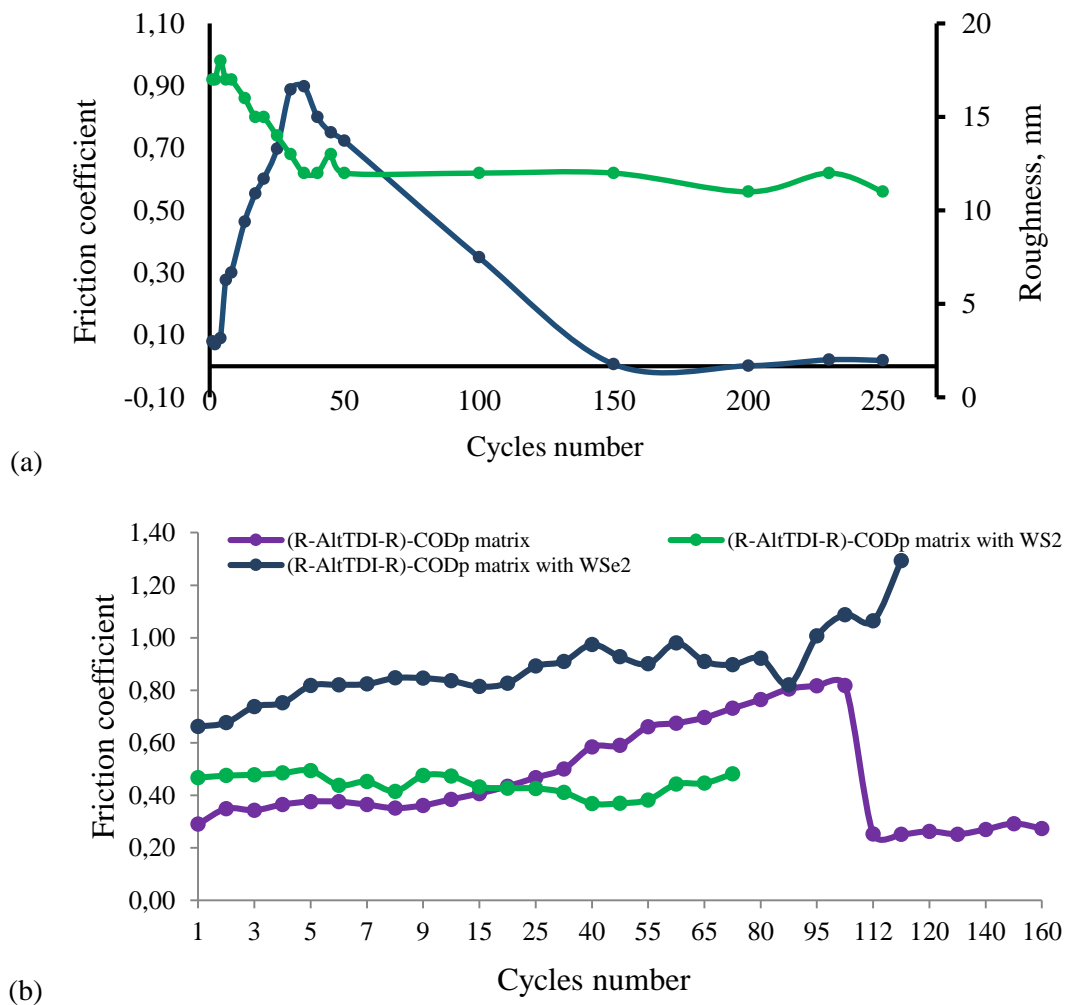
Figure 5. Dependence of the friction coefficient on the number of scanning cycles during multipass AFM testing: (a) 20°C, F normal 175 nN, friction forces 10-160 nN. Green curve – roughness, blue curve – C_{fr}; (b) (R-AltTDI-R)SOD*p* matrix (30°C, F normal 45 nN, friction forces 14-12 nN), with WS_2 (20°C and F normal 48 nN, friction forces 45-65 nN), with WSe_2 (30°C, F normal 54 nN, friction forces 30-60 nN).
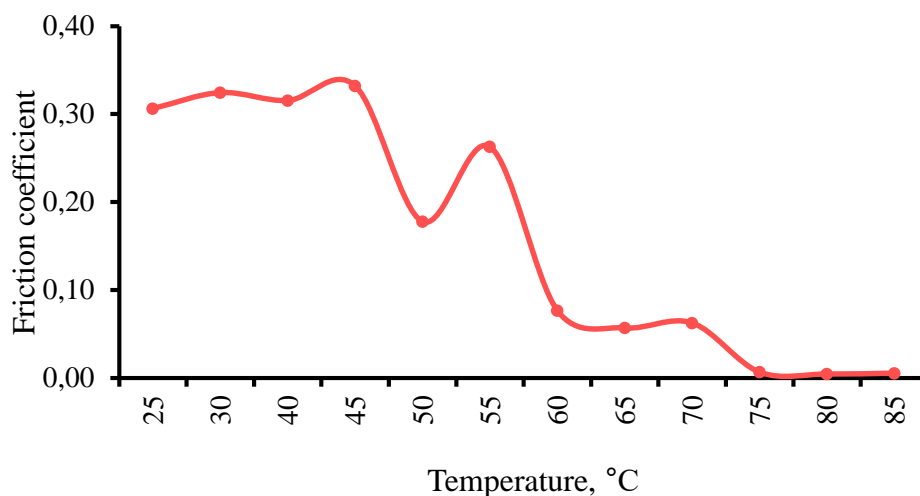
Figure 6. Dependence of the friction coefficient on the temperature during tribological AFM testing of (R-AltTDI-R)SOD*p* matrix with WS$_2$ with thermal platform under heating from 25 to 85°C (F normal = 69 nN, friction forces = 1-60 nN).

The significant difference in the topography of the opposite films surfaces leads to a significant difference in roughness (Table 2). (R-2300TDI-R)SOD*p* + 1% Graphene and (R-2300TDI-R)SOD*p* + 1% SWCNT films have the close roughness values on the opposite sides. The roughness of (R-2300TDI-R)SOD*p* + 1% VGCF films and all films of nanocomposites based on (R-AltTDI-R)SOD*p* matrix differ by two or three times. Thus, additives and substrates significantly influence on the structure formation of these PI films and on the properties of their surfaces.

C$_{fr}$ of matrices without additives differ threefold: 0.164-0.167 for (R-2300TDI-R)SOD*p* and 0.056-0.065 for (R-AltTDI-R)SOD*p*. The addition of VGCF reduces C$_{fr}$ of (R-2300TDI-R)SOD*p* matrix more than twice to 0.061-0.074 and leaves C$_{fr}$ of (R-AltTDI-R)SOD*p* matrix at the low level about 0.066-0.071.The addition of SWCNT practically leaves C$_{fr}$ of both matrices on the level of C$_{fr}$ of pure matrices. The addition of graphene increases C$_{fr}$ of both matrices, especially that of (R-2300TDI-R)SOD*p*. Thus, only the addition of VGCF to (R-2300TDI-R) SOD*p* matrix improves the tribological properties of the surface. The excess of the quantity necessary for the modification, as in the case of coPUI with 10% graphene, can substantially worsen the surface properties.

In general, WS$_2$ and WSe$_2$ nanoparticles degrade C$_{fr}$ of the (R-2300TDI-R)SOD*p* and (R-AltTDI-R)SOD*p* matrices due to a significant increase of roughness. WSe$_2$ decreases twice the C$_{fr}$ of (R-AltTDI-R)SOD*p* matrix surface formed on glass.

The dependences of roughness and C$_{fr}$ value on the number of scans during multipass tribological AFM testing of (R-AltTDI-R)-CODp matrix are presented on Figure 5a. This measurement was performed at 20°C and normal load about 175 nN. Friction forces ranged from 10 to 160 nN. Each point on the C$_{fr}$ graph (blue) and the roughness graph (green) is obtained from a separate AFM sequential scanning field (Fig. 5). At the initial stage of C$_{fr}$ graph up to 50 cycles, the growth of C$_{fr}$ to 0.9 was determined and the roughness simultaneously decreased. When the probe moves along the surface, the roughness is smoothed out. The low initial value of C$_{fr}$ 0.1 can be attributed to developed roughness when the probe contacts with surface along the tops of the irregularities. In this case, the frictional forces are lower than those for the contact of the smoothed sample with entire surface of the probe. The energy should be spent on the process of smoothing and it is necessary to apply a greater lateral force for further movement [2]. Therefore, K$_{tr}$ grows on this site. In the process of friction, the irregularities are smoothed out and after reaching the minimum of roughness, C$_{fr}$ decreases over the next 100 cycles to a stable value of 0.05. And then the mechanism of elastic non-wear friction works.

When the same multipass tests are repeated at 30°C, the probe-sample contact conditions change, which raises the initial value of C$_{fr}$ to 0.3 instead of 0.1 at 20°C (Fig. 5b). The normal load was about 116 nN and measured friction forces in a range of 30-92 nN. C$_{fr}$ is stable at the beginning during the

first 10 cycles and then it increases smoothly. After reaching 0.8 at 110 cycles as well as at 20°C the curve decreases to a stable level 0.25. The testing at 30°C places peculiarities on the C_{fr} graph: growth is smoother and decrease is faster. The results of friction change during multipass tribological AFM testing at 30°C of (R-AltTDI-R)SODp matrix with WS_2 and WSe_2 nanoparticles are shown on Figure 5b. As for pure (R-AltTDI-R)SODp matrix the results of testing at higher temperature show the increased C_{fr} in comparison with the testing at 30°C. The addition of WS_2 nanoparticles keeps C_{fr} stable on the level 0.45. The addition of WSe_2 nanoparticles leads to C_{fr} increase.

The influence of heating on C_{fr} of (R-AltTDI-R)SODp with WSe_2 is shown in Figure 6. C_{fr} is stable till 45°C. Then it dramatically decreases at 60°C and keeps stable till 70°C, while at 75°C it decreases. Comparing the similar values of C_{fr} of (R-AltTDI-R)SODp matrix determined for «multipass scan» and «one scan under heating», it should be noticed that the influence of heating from 75 to 85°C on the surface properties is similar to the influence of 200-400 testing scans at 20°C. This fact allows us to conclude that heating in this micro contact is equal to 75°C. These results show that synthesized coPUI films are very promising for tribological applications and their properties can be controlled both by temperature and mechanical action.

4. Conclusion
The tribological properties of new thermoplastic elastomers based on (R-AltTDI-R)SODp and (R-2300TDI-R)SODp coPUI matrices modified with carbon materials (nanotubes, graphene, and fibers) were tested in microscale by atomic force microscopy.

Comparing the similar values of C_{fr} of (R-AltTDI-R)SODp matrix determined in regimes «multipass scan» and «one scan under heating», it should be noticed that the influence of heating in the range of 75-85 °C on the surface properties is similar to the influence of 200-400 scans of multipass testing at 20 °C. This fact allows making a conclusion that there is a heating in this micro contact equal to 75 °C. These results show that synthesized coPUI films and nanocomposites based on them are very promising materials for tribological applications and their properties can be controlled both by temperature and by mechanical action.

It is shown that the addition of carbon materials to the studied films significantly changes their friction coefficient due to extreme sensitivity of coPUI matrices to the synthesis conditions, solvent evaporation rate, and surface effects. Thus, the friction coefficient can be controlled by the addition as well.

Therefore, it is shown that atomic force microscopy is an excellent research tool in the field of tribology in nanoscale.

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