ISSN 0012-5008, Doklady Chemistry, 2016, Vol. 466, Part 2, pp. 25–28. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © V.A. Beloshenko, A.V. Voznyak, Yu.V. Voznyak, A.V. Kupreev, 2016, published in Doklady Akademii Nauk, 2016, Vol. 466, No. 4, pp. 430–433.

CHEMISTRY

Tribological Properties of an Antifriction Polymer Modified by Severe Plastic Deformation

V. A. Beloshenko[a], A. V. Voznyak[b], Yu. V. Voznyak[c], and A. V. Kupreev[d]

Presented by Academician Al.Al. Berlin July 8, 2015

Received July 8, 2015

Abstract—The possibility of applying severe plastic deformation technologies to improving the tribological characteristics of semicrystalline antifriction polymers was studied. By the example of Nylon 6 subjected to equal-channel multiple angular extrusion, it was shown that severe plastic deformation favors a significant (more than three orders of magnitude) increase in the wear resistance of polymer and a 15–20% decrease in its friction coefficient. There are also increases in the maximum allowable contact pressure and temperature in the friction zone, at which the wear and the friction coefficients are stable.

DOI: 10.1134/S0012500816020026

A conventional method for controlling the tribological characteristics of both thermoplastics and thermosets is to fill them with various nano- or micromodifiers [1]. This problem is generally solved by complex experimental selection of polymer matrices and contents and types of modifying additives to make a tradeoff between the main tribological parameters: friction coefficient, wear resistance, and bearing ability of rubbing surfaces. Such an approach allows one to create composite materials far superior in properties to base polymers, but requires one to perform much investigation because of the necessity to ensure the controllable action of fillers on various levels of the structural organization of the polymer matrix.

Another method is radiation modification, which improves the tribological properties of polymers owing to cross-linking of polymer chains [2, 3]. However, this method is not always efficient. In some cases, improvement of tribological characteristics is reached by a change in the initial molecular and/or supermolecular structure [4, 5]. The advantage of unfilled polymer materials is the simplicity of their production, whereas their disadvantages are relatively low values of allowable pressure and wear resistance.

An alternative solution of the problem of improving antiwear properties of materials while preserving their antifriction properties can be severe plastic deformation technologies. It was determined [6, 7] that one of the severe plastic deformation technologies, equal-channel multiple angular extrusion (ECMAE), yields semicrystalline polymer products with high strain–strength properties and new functional characteristics. In particular, while their plasticity is preserved on the level of the initial material, their hardness and strength are higher by a factor of 2–7 and are slightly anisotropic, and a biaxial invar effect is also observed (very low $-(5–7) \times 10^{-6}$ K^{-1} and slightly varying values of the linear thermal expansion coefficient over a wide temperature range). The obtained result is due to the formation of a biaxially oriented structure consisting of a network of intertangled fibrils, which is aligned with the extrudate axis. In this case, one can expect a synergistic effect of improvement of the strain–strength and tribological properties of extruded polymers.

In this work, this was demonstrated for the first time by the example of Nylon 6, which is widely used as an antifriction polymer material.

In ECMAE, a cylindrical polymer extrusion billet is forced through a die that has several channels of the same diameter, which intersect at given angles [8]. In a die used in this work, inclined extrusion channels could be alternated with vertical ones, and simple shear could be performed with varying the spatial orientation of the simple shear direction and the shear planes, i.e., along various deformation routes [6]. We

[a] *Galkin Donetsk Physicotechnical Institute, National Academy of Sciences of Ukraine, pr. Nauki 46, Kyiv, 03028 Ukraine*
[b] *Tugan-Baranovskii Donetsk National University of Economics and Trade, ul. Kurchatova 13, Kryvyi Rih, 50042 Ukraine*
[c] *Center for Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, Lodz, 90-363 Poland*
[d] *Belyi Institute of Mechanics of Metal–Polymer Systems, National Academy of Sciences of Belarus, ul. Kirova 32a, Gomel, 246050 Belarus*
e-mail: biloshenko_va@mail.ru; wozniak@cbmm.lodz.pl

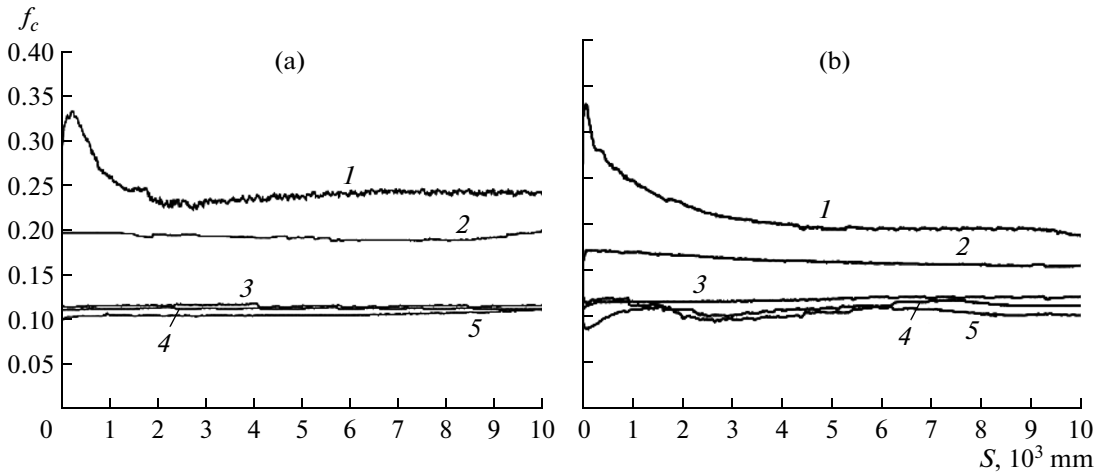

Fig. 1. Dependence of the friction coefficient f_c of the (a) initial and (b) ECMAE-modified Nylon 6 specimens on the rubbing path at loads of (*1*) 100, (*2*) 250, (*3*) 500, (*4*) 750, and (*5*) 1000 mN.

chose the D + C deformation route, in which pairwise connected inclined deformation channels lie in perpendicular planes rotated around the vertical axis at a pitch of 90° and are separated by vertical channels (see detailed description in [7]). Tests were made on commercial rod specimens of Nylon 6 (Ertalon 6 SA, Quadrant). The extrusion rate was 0.6×10^{-3} m/s, the extrusion temperature was 150°C, the cumulative strain was $\varepsilon = 8.5$, and the strain rate was $\Delta\Gamma_1 = 0.83$, which corresponded to the optimum process conditions [6].

The friction coefficient f_c was determined with an MTU-2K7 reciprocating microtribometer [9]. The tests were performed under normal conditions according to the GOST (State Standard) 8.395-80 without lubricant. The counterbody was a ShKh15 steel 4.7 mm in diameter. The tests were carried out at loads of 100, 250, 500, 750, and 1000 mN, a relative rubbing velocity of 2.5 mm/s, a double stroke length of 10 mm, and a rubbing path of 10.0 m.

The linear wear rate of materials was estimated by testing on a 2070 SMT-1 friction and wear testing machine (shaft–sleeve friction pair). The pressure at the friction joint was varied within the range 0.25–2.75 MPa, and the linear rubbing velocity was 0.5 m/s. The material of the counterbody is steel 45 (GOST 1050-88) with a hardness of 45–48 HRC and a surface roughness of $R_a = 0.32$ μm. The coefficient of mutual overlap of the shaft–sleeve friction pair was 0.125. Wearing-in was performed at a pressure of 0.25 MPa and a rubbing velocity of 0.5 m/s until a contact formed throughout the friction surface. The friction temperature of the specimen was monitored with a chromel–copel thermocouple at a distance of 1 mm from the friction surface.

The absolute linear wear rate was found as

$$I_h = \frac{\Delta m}{\rho S_a L},$$

where Δm is the wear of the material in time Δt, g; ρ is the density of the material being worn, g/cm^3; S_a is the friction surface area of the piece being worn, cm^2; and L is the rubbing path, cm. L was calculated as

$$L = v\Delta t,$$

where v is the rubbing velocity, cm/s; Δt is the wear time, s.

Figure 1 illustrates the dependence of the friction coefficient f_c of Nylon 6 on the rubbing path. It is seen that f_c varies with time similarly for both the initial Nylon 6, and the polymer subjected to ECMAE. However, in the deformed Nylon 6, equilibrium f_c values are established half as fast as and their magnitudes at a rubbing path of 8–10 m are lower than those in the initial polymer (Table 1). The difference in dynamics of the change in the friction coefficient can be due to features of structural rearrangements in the initial and oriented polymer on the surface of the friction contact. In the first case, f_c rapidly plateaus, which indicates the completion of processes of the formation of the so-called transfer film and the orientation of polymer chains on the surface of the specimen along the slip direction. In the second case, equilibrium f_c values are established for a longer time because of the necessity of reorientation of ECMAE-modified, biaxially oriented molecular chains in the slip direction.

ECMAE also influences the wear resistance of Nylon 6 (Table 2). The linear wear rates I of the initial Nylon 6 and the ECMAE-modified polymer increase with increasing loads at low loads (0.25–1.25 MPa). With a further increase in the contact pressure, the

wear rate of the initial polymer abruptly increases, whereas I of the deformed polymer does not significantly change throughout the studied load range. Note also the fact that the deformed specimens can withstand much higher contact loads for longer loading times (Table 2).

It is known that there exist two wear mechanisms, which differ in scale of delaminated (decomposing) structures: the mild wear mechanism involving the pulling of fibrils from lamellar structures of crystallizing polymers and the severe wear mechanism based on the development of lamination wear similar to the process described in the delamination theory of wear [10]. Lower wear resistance at low loads and extremely high wear resistance at high loads of the deformed Nylon 6 in comparison with the initial polymer are indicative of the formation of a structure that favors the mild wear mechanism and inhibits the severe wear mechanism.

Our results demonstrated [6, 7, 11, 12] that ECMAE leads to a decrease in the porosity, and also to the destruction of the lamellar structure and to the formation of a fibril network oriented along and perpendicular to the longitudinal axis of an extrudate. ECMAE-modified polymers have higher crystallinity and larger crystallites [13]. One can assume that the lower wear resistance of the Nylon 6 extrudates at low loads is due to the abrasive mechanism of wear, which is caused by the presence of larger crystallites, by a lower fraction of the amorphous phase, which reduces the mobility of crystallites and complicates their reorientation in friction, and by the presence of fibrils perpendicular to the friction surface. The elevated rigidity of extrudates improves the wear resistance at high loads. It is known that an increase in the wear of polymers correlates with their yield point [14], which for the ECMAE-modified Nylon 6 exceeds that of the initial polymer by a factor of 2–2.5 [6].

It is also seen from Table 2 that the wear rate of the deformed Nylon 6 also changes weakly at elevated temperatures in the friction zone (up to 180°C). Such a behavior can be brought about by high heat resistance of extrudates. As we showed previously [6], this is related to the formation of fibrils forming a dense network of physical nodes, which favors an increase in the heat resistance of deformed polymers [15]. The fact that the wear rates of the deformed polymers are low and vary weakly at elevated temperatures demonstrates their stability in the contact region and a low intensity of the removal of the polymer material from the tribo-contact region, which suggests their high heat resistance.

Thus, severe plastic deformation by equal-channel multiple angular extrusion is a promising approach to creating antifriction polymer materials with improved wear resistance, load capacity (high allowable contact pressure), and heat resistance. It was shown by the example of Nylon 6 that ECMAE causes a decrease in the friction coefficient by 15–20% and in the linear wear rate by three orders of magnitude at high loads (1.75–2.75 MPa) in comparison with the initial polymer. In this case, the maximum allowable working pressure doubles and the reached linear wear rates are preserved also at elevated temperatures.

Table 1. Effect of ECMAE on the established values of the friction coefficient of Nylon 6 at a rubbing path of 8–10 m

Load, mN	f_c	
	initial	after ECMAE
100	0.242–0.244	0.192–0.204
250	0.194–0.198	0.158–0.162
500	0.115–0.118	0.114–0.117
750	0.112–0.117	0.109–0.114
1000	0.107–0.111	0.101–0.105

Table 2. Effect of ECMAE on the linear wear rate of Nylon 6 at a wear time of 3600 s

Nylon 6	Pressure, MPa	Specimen temperature at end of test, °C	Linear wear rate, 10^{-8}
Initial	0.25	43	0.28
	0.5	57	0.39
	0.75	117	1.38
	1.0	102	0.83
	1.25	147	6.34
	1.5	163*	3800.9*
After ECMAE	0.25	45	0.39
	0.5	113	1.61
	0.75	145	3.02
	1.0	147	1.61
	1.25	155	1.90
	1.5	150	2.14
	1.75	147	2.39
	2.0	160	1.95
	2.25	172	4.09
	2.5	162	5.60
	2.75	180	6.67

* The wear time is 540 s.

REFERENCES

1. Pesetskii, S.S., Bogdanovich, S.P., and Myshkin, N.K., *Trenie Iznos,* 2007, vol. 28, no. 5, pp. 500–524.

2. Briscoe, B.J. and Ni, Z., *Wear*, 1984, vol. 100, pp. 221–292.
3. Burroughs, B.R. and Blanchet, T.A., *Tribol. Trans.*, 2001, vol. 44, no. 2, pp. 215–223.
4. Pooley, C. and Tabor, D., *Proc. R. Soc. London, A*, 1972, vol. 329, no. 1578, pp. 251–274.
5. Myo, M. and Sujeet, K.S., *Tribol. Lett.*, 2009, vol. 34, pp. 133–140.
6. Beloshenko, V.A., Voznyak, Yu.V., Reshidova, I.Yu., Nait-Abdelaziz, M., and Zairi, F., *J. Polym. Res.*, 2013, vol. 20, p. 322.
7. Beloshenko, V.A., Voznyak, A.V., and Voznyak, Yu.V., *Polym. Eng. Sci.*, 2014, vol. 54, pp. 531–539.
8. Beloshenko, V.A., Varyukhin, V.N., Voznyak, A.V., and Voznyak, Yu.V., *Dokl. Phys. Chem.*, 2009, vol. 426, part 1, pp. 81–83.
9. Semenyuk, M.S., Zozulya, A.P., Kudritskii, V.G., Grigor'ev, A.Ya., Myshkin, N.K., et al., RF Patent No. 5089, *Byull. Izobret.*, No. 1 (2010).
10. Suh, N., *Wear*, 1973, vol. 25, no. 1, pp. 111–124.
11. Beloshenko, V.A., Voznyak, A.V., Voznyak, Yu.V., and Dudarenko, G.V., *J. Appl. Polym. Sci.*, 2013, vol. 127, pp. 1377–1386.
12. Beloshenko, V.A., Varyukhin, V.N., Voznyak, A.V., and Voznyak, Yu.V., *J. Appl. Polym. Sci.,* 2012, vol. 126, pp. 837–844.
13. Beloshenko, V.A., Voznyak, Yu.V., and Mikhal'-chuk, V.M., *Vysokomol. Soedin., Ser. A*, 2014, vol. 56, no. 3, pp. 269–275.
14. Yamaguchi, Y., *Tribol. Ser.,* 1990, vol. 16, pp. 143–155.
15. Beloshenko, V.A., Varyukhin, V.N., and Voznyak, Yu.V., *Strukturnaya modifikatsiya polimernykh materialov metodami tverdofaznoi ekstruzii* (Structural Modification of Polymeric Materials by Solid Phase Extrusion), Saarbrucken: LAP LAMBERT Academic Publ., 2014.

Translated by V. Glyanchenko