

IMPROVED TECHNIQUES FOR OBTAINING POLYMER-NANODIAMOND COMPOSITES WITH ENHANCED PROPERTIES

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ABSTRACT

Several methods were developed to improve distribution of detonation nanodiamond (ND) particles in thermoplastic polymers: polysulfone (PSF) and copolymer of acrylonitrile and styrene (SAN). The morphology and dynamic mechanical properties of polymer-nanodiamond nanocomposites were investigated. From optical and transmission electron microscopy (TEM) analysis of the nanocomposites with ND, it was observed that majority of the ND aggregates are less than 100 nm. Investigation of dynamic mechanical properties of the polymer-nanodiamond composites showed that the storage modulus in rubbery state was increased by addition of the ND. Stress-strain tensile properties and Izod impact strength of polymer/ND composites were investigated. The introduction of ND in the polymer matrixes results in not only to reinforcing of commodity polymers, but also to improvement of their tribological properties.

1. INTRODUCTION

Introduction of nanoparticles in polymer can lead to improvement engineering properties and to appearance of new functional properties to large-capacity polymers. When fillers are nanoscopic, there are advantages afforded to filled polymers and composites that lead to performance enhancements. These advantages results primarily from filler size reduction and the concomitant increase in surface area. It means, that creation of materials with unique or improved properties will not demand creation of new chemical manufactures for production of new and, as a rule, expensive polymers. For this reason the high activity of various research groups in the field of detail investigation of structure and properties of nanoparticles of different nature and composite materials on their basis now is being observed. Nanodiamonds of detonation synthesis has become one of the most important materials for science and technology due to their superior properties such as hardness, wear resistance, chemical inertness, low electrical conductivity, high conduction of heat and other [1, 2]. The final properties of the polymer/ND nanocomposites, such as mechanical and thermal properties, are highly dependent on the dispersion degree of the ND particles. Their high surface energy and presence of interacting functional groups on the surfaces leads to agglomeration of individual particles. That is why homogeneous distribution especially of small amounts of filler is a huge and very important problem. In a previous work [3] it was shown that extended approaches for producing of polymer nanocomposites from melt blend and by "solvent" method (dissolving and casting) do not allow to achieve high filler dispersity in a polymeric matrix. As earlier was established [4], the shear flow of heterogeneous systems (viscoelastic media/nanofiller) results in aggregation (sometimes, ordering) of particles. Since most of composites based on thermoplastics

and dispersed fillers are produced by melt mixing-extrusion procedure, the simple shear is not capable to solve a problem of nanoparticles disagglomeration. The modified mixer was developed for the solution of this problem and manufacturing conditions for composites with high filler dispersity were proposed.

2. EXPERIMENT

Materials

Detonation nanodiamonds were synthesized by “Electrohimpribor”, Russia, (trade mark “PUOO-SH – 96”), weight fraction of ND in a powder is not less than 98 %, density is 3.3 g/cm^3 , specific surface is $350 \text{ m}^2/\text{g}$. The following materials were used as a polymer matrix: copolymer of acrylonitrile and styrene (SAN) - transparent granules (trade mark M100 by Bayer, Germany), M_w 175000, acrylonitrile contain 30%, density $1.07\text{-}1.08 \text{ g/cm}^3$; and polysulfone (PSF) as white powder (trade mark PSK-1 by “Research Institute of Polymer Materials”, Russia).

Preparation of polymer/ND composites

The SAN pellets was dried under vacuum at 80°C for 4 h, and PSF and ND powders were dried at 120°C for 10 h before processing. For development and comprehensive study of polymer nanocomposites the new laboratory equipment for thermoplastic composite processing was designed and constructed. This multipurpose device based on standard capillary viscometer working with a few grams of polymer can be used as the single-screw miniextruder for mixing extrusion processing. Standard mixing is carried out throughout 7 minutes at temperatures: $200\text{-}220^\circ$ (for SAN) and $280\text{-}300^\circ \text{C}$ (for PSF) and 60-80 rpm. Using this equipment it was possible to realize the offered concept of rheological dispersing mixing in “spurt” regime where irregular streams turbulence vortexes and fluctuating cavitation zones lead to crushing of ND aggregates. In this case mixing procedure was realized at the same conditions but at high speed of screw rotation (600-800 rpm). By this way, composites with ND content from 0.25 to 10 wt.% were prepared.

Dispersion of ND in polymers

For definition of grain size distribution of ND particles in polymeric matrixes used optical microscopy (microscope MIN-8 supplied with the digital camera) and TEM (Zeiss LEO 912AB OMEGA). Calculation of particles distribution carried out by computer processing of digital photos. All program complex of processing of the image is realized by means of mathematical computer program pack MathLab.

Mechanical and thermomechanical properties

Mechanical properties of extruded samples of the circle cross-section were measured on tensile machine Instron 1122 at extension rate of 10 mm/min . The notched samples of PSF/ND composites have been tested for Izod impact strength by standard methodic. The dynamic mechanical analysis of composites has been carried out on torsion pendulum in the field of temperatures $20\text{-}160^\circ\text{C}$ (in the case of SAN matrix) and $20\text{-}250^\circ\text{C}$ (in the case of PSF matrix) in the conditions of dynamic low-amplitude deformations at frequency 25 - 27 Hz. The temperature was scanned at a rate of 0.5°C/min .

Tribological properties

By means of an original technique the sliding friction coefficient and wear resistance of composites on nichrome has been measured. Principle of tribometer working is following: in the holder of horizontally fixed microdrill the tested sample (extrudate) contacting with the counterface (nichrome wire, $d = 50 \mu\text{m}$) on whole radius (angle of contact of the sample by wire is 2π); to vertically suspended wire from below moves loading (certain weight), the top end of the wire is fixed to detecting device fixing change of loading in the process of the friction. Speed of rotation of the microdrill corresponds to linear speed of wire sliding 1 m/min. The coefficient was calculated using Euler's formula.

$$S_0 = S \cdot e^{f\alpha} \quad (1)$$

Here S_0 – loading, S – strain, f – friction coefficient, α – angle of contact of specimen by wire.

3. EXPERIMENTAL RESULTS

3.1 Dispersion of ND in polymers

The dispersion of ND in polymer matrix is one of the most important questions for fabricating high-performance composites. For comparison the results of two methods of the filler introduction (obtained by standard melt-mixing and mixing in “spurt” regime) for compositions at SAN example optical images are shown in figure 1.

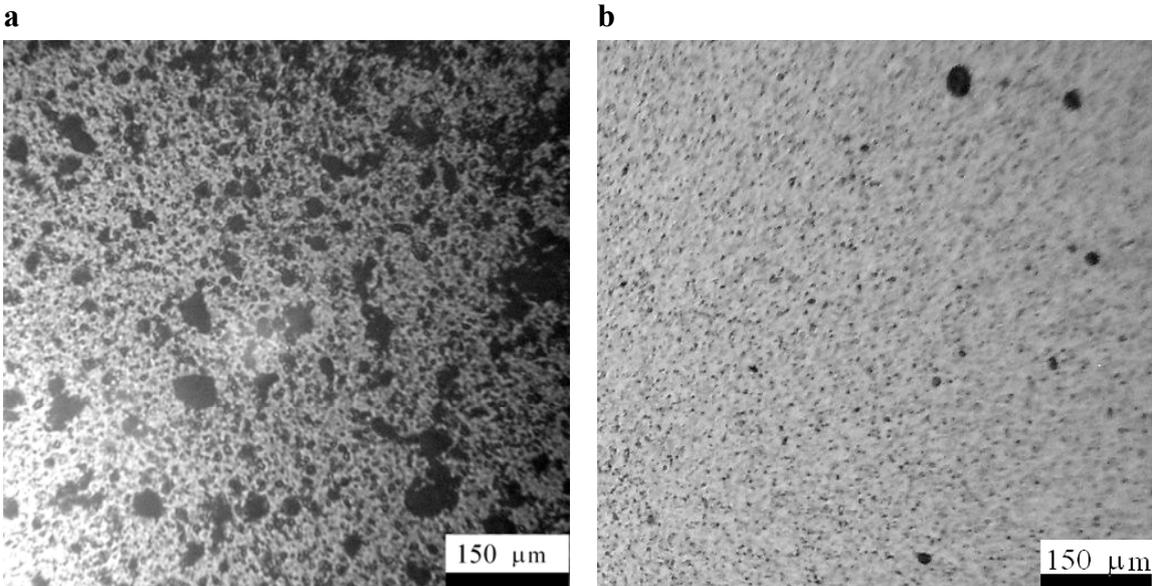


Figure 1: Optical images of composites SAN/1 wt.% ND obtained by standard melt-mixing (a) and mixing in “spurt” regime (b).

Obviously, the whole dispersion of ND in composites, obtained by melt-mixing in “spurt” regime, is more homogeneous. Optical microscopy can be used to observe big agglomerates of ND but is incapable to analyze the dispersion of single ND particle at the nanoscale. TEM of thin section has the advantage of showing all segments of ND

located within the thickness of the section. A TEM micrographs of the SAN/ND nanocomposites with 1 wt.% ND content is shown in figure 2.

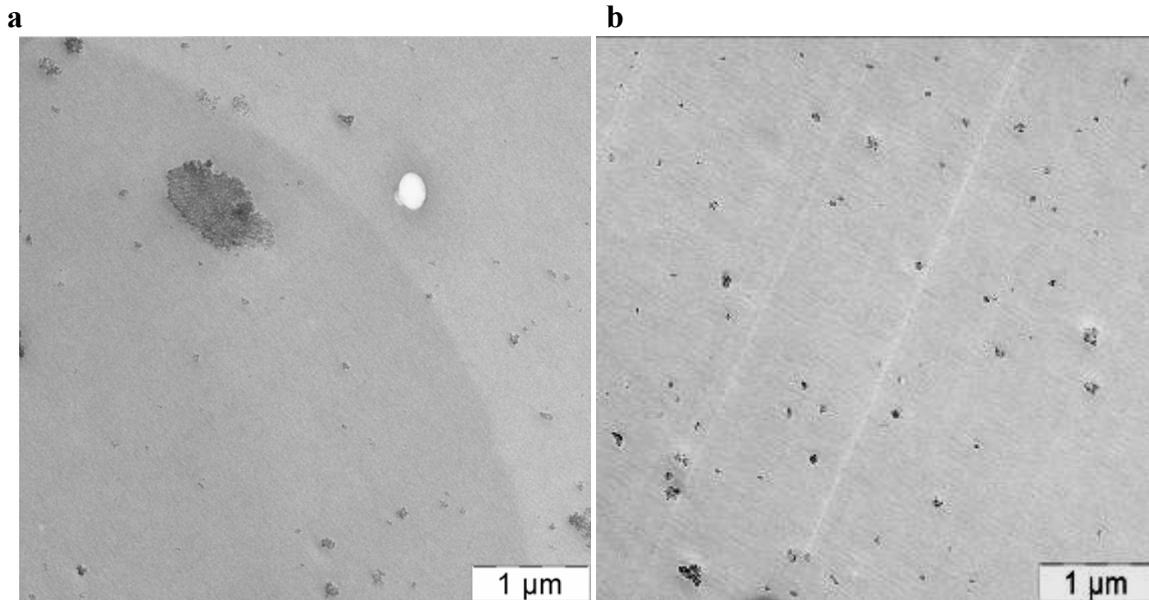


Figure 2: TEM images of composites SAN/1 wt.% ND obtained by standard melt-mixing (a) and mixing in “spurt” regime (b).

As it seen, at submicron level nanodiamond particles more uniformly dispersed in the composite, obtained via melt-mixing in “spurt” regime, although slight particle aggregation takes place. Having compared the data of particles distribution in micron and submicron area the generalized polydispersity curve was graphed. Curve for composite SAN/ND (1 wt.%) prepared via melt mixing on “spurt” regime is shown in figure 3. Apparently a main part of ND aggregates are less than 100 nm.

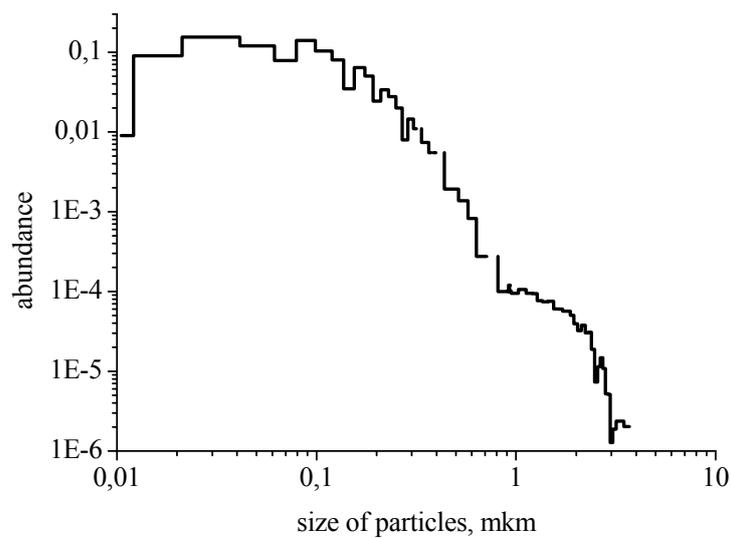


Figure 2: Generalized polydispersity curve of SAN/1 wt.% ND.

3.2 Mechanical and thermomechanical properties

The best tensile properties were achieved for composites obtained by melt-mixing in “spurt” regime. Maximal values of SAN, PSF (neat polymers were treated in the conditions of composites preparing) and the nanocomposites are presented at table 1.

Table 1: Tensile properties of polymer-ND composites obtained by melt-mixing in “spurt” regime.

Parameter	Polymer matrix	ND content, wt. %	Value
Young modulus, G_{max} , GPa	SAN	0	2.12
		2.5	2.95
	PSF	0	1
		5	1.9
Tensile strength, σ_{max} , MPa	SAN	0	46
		0.5	65
	PSF	0	103
		0.25	150
Elongation at break, ϵ , %	SAN	0	3
		0.5	3.6
	PSF	0	32
		0.5	74

The basic tensile properties of the composites were improved evidently. The optimal filler content is 0.5% by weight. Increases in Young modulus and strength indicate that nanodiamonds are acting as reinforcement in the polymer matrix by transferring load from the polymer to the ND. The decreasing of mechanical characteristics of the composites obtained by a standard melt-mixing, explains by presence of a considerable quantity of the big agglomerates acting as a defects of the system.

Composites PSF/ND has been tested for impact strength. Figure 3 shows the influence of ND concentration and way of composite obtaining on impact strength.

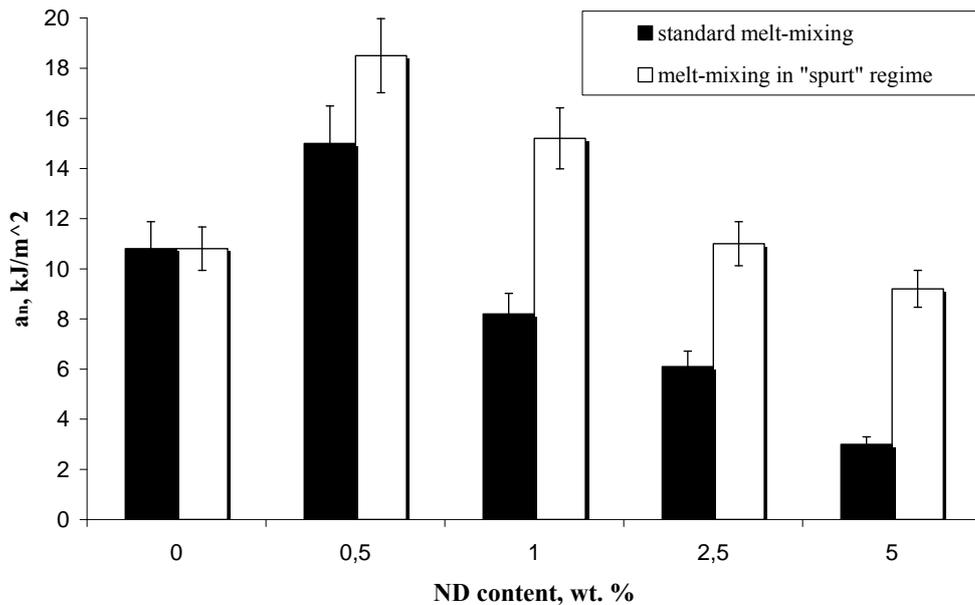


Figure 3: Izod impact strength of PSF/ND composites manufactured by different ways.

As it seen already 0.5 wt.% of ND results in increment of impact strength almost in 2 times. Composites prepared by standard melt-mixing possess essentially the worst properties. This can be attributed to poor uniformity of the ND distribution in the polymer matrix. The mechanism of strength increasing at nanoparticles introduction is connected to effect of increase in surface energy of breaking due to deviation of a crack and origin of plastic deformations in the field of particles and matrix contact.

The fact of decreasing of physical-mechanical characteristics at 5 wt.% of ND can be explained to that at addition of a lot of the filler having developed surface, the level of residual stresses on a polymer-particle interface increases. Also increases a faultiness caused by the presence in the system large aggregates at high filler concentration.

Temperature dependences of dynamic mechanical properties of composites by means of torsion pendulum have been investigated.

Loss factor ($\tan \delta$) of the systems in the entire testing temperature range differ slightly – with the increasing of ND concentration up to 10 wt.% $\tan \delta$ rather more than that of virgin polymer. The height of the $\tan \delta$ peak of the PSF/ND composites was decreased from 4.6 to 3.8 when the ND concentration was increased up to 10 wt.%. The storage modulus of the composites which are in a glassy state practically does not depend on concentration of the ND. But in the field of glass transition and in rubber-like elasticity region the modulus G' of composites considerably exceeds the corresponding value of the neat polymer. Already the introduction of 1 wt.% of ND leads to doubled of this characteristic (figure 4). So the ND leads to the change in the nature of the molecular motion in the bulk material of PSF.

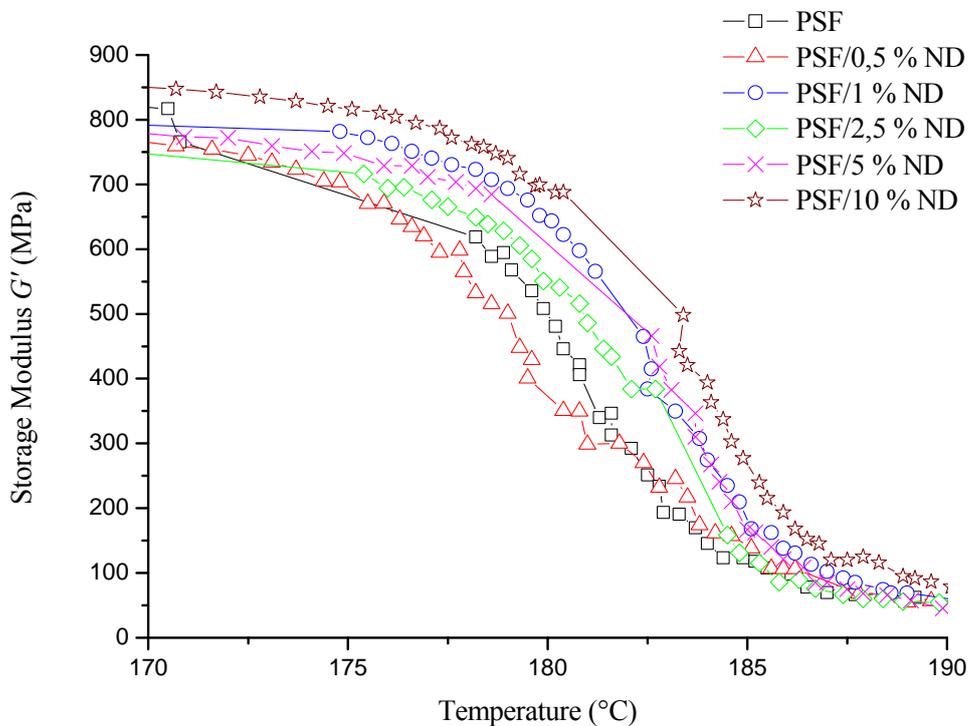


Figure 4: Variation of storage modulus with temperature for the PSF/ND composites (manufactured by melt-mixing in “spurt” regime).

Addition of the ND results in to insignificant growth of glass transition temperature (10 wt.% content of ND in polysulfone leads to increasing of T_g on 4-5°C). The increase of the T_g of the polymer-ND nanocomposites suggests that the polymer chain motion is restricted by the ND particles. More interesting the fact of T_g decreasing at the small filler content (0.5 wt.% of ND in polysulfone reduce T_g on 3°C, and in case of the SAN-matrix more essential decreasing at 5-6°C was observed). Strong adhesion between nanoparticles and surrounding polymer matrix additionally enhances the dynamic modulus and T_g by reducing molecular flexibility to some extend. The hard particles incorporated into the polymer would act as additional virtual network.

3.3 Tribological properties

At the beginning of the running-in stage, the sliding performance is similar for all compositions. But, the frictional coefficient were abruptly increased after an initial stage of the contact period (in our case is 2-5 min) due to formation of tranferred film of polymer. The effect of ND addition to PSF on sliding friction coefficient is shown in figure 4. Nanocomposites with ND exhibited a less steady state coefficient of friction compared with the pristine PSF.

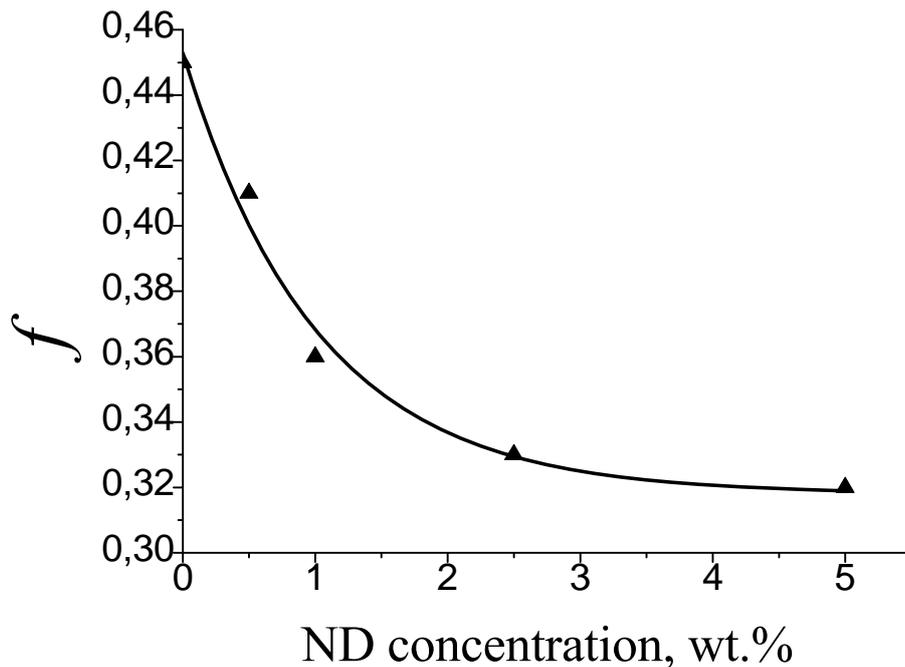


Figure 5: Friction coefficient of PSF and PSF-ND nanocomposites. Wear conditions: sliding velocity -1 m/s, duration – 15 min.

Figure 6 shows the micrographs of the abraded surface of polysulfone and polysulfone nanocomposites (scaled up area of extrudate's side). By incorporating ND wear is significantly reduce. Hard nanodiamond particles provide protection and prevent the polymer matrix from severe wear.

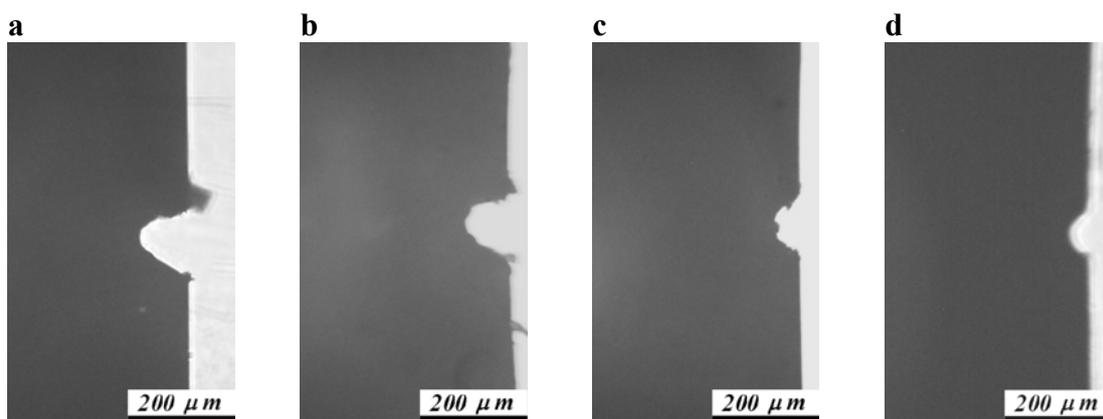


Figure 6: OM micrographs of the worn surfaces of the PSF-ND nanocomposites: neat PSF (a), PSF/1 wt.% ND (b), PSF/2.5 wt.% ND (c), PSF/5 wt.% ND (d). Wear conditions: sliding velocity -1 m/s, duration – 15 min.

4. CONCLUSIONS

By the studies of the optical microscopy and TEM, the significant improving of ND dispersion in the polymer matrix was in the composites obtained by melt-mixing in “spurt” regime. The nanodiamond particles incorporated into the polymer matrix generate remarkable improvements in material characteristics. From the results of the dynamic mechanical properties of the polymer-ND nanocomposites, the storage modulus was increased by the addition of the ND at the rubbery state. Modification of polymers by ND leads to improvement of their mechanical and tribological characteristics. As low as 0.5 wt.% ND in PSF results in almost a twofold increase in impact strength. Mechanical properties of composites obtained via melt-mixing in the conditions of "spurt" are enhanced significantly compared with those for standard mechanical melt-mixing. Significant improvements of the wear resistance and decreasing of friction coefficient of polymers were achieved at very low filler content (1-5 wt.%).

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