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## The physicochemical characterization of fluoropolymer-modified polysiloxane coatings

**Summary** — A polymer hybrid system, containing a crosslinked polysiloxane (SIL) and fluoropolymer (PTFE), was developed and it has been applied as the antigraffiti coatings. Surface physicochemical properties of the system were investigated, using the tensiometry to determine surface wetting properties, such as the dynamic contact angle (DCA), the X-ray photoelectron spectroscopy for the surface chemical analysis (ESCA/XPS), and the atomic force microscopy (AFM) to observe the surface morphology and roughness. Then, the surface free energy (SFE) and its polar and dispersive parts were calculated from DCA data, as well as the surface elemental composition: F, C, Si, O, in particular the Si and F atoms distributions in the surface layers (XPS), and the roughness parameters of the surface (AFM). It has been found that the following factors are crucial for applications of the SIL/PTFE system as coatings for permanent protection of building materials against graffiti paintings: (a) the wettability, it should be low, (b) the chemical composition, an excess of F atoms at the surface is required, (c) the morphology of surface layers, *i.e.*, tightly packed small domains and the low roughness. Optimum hydrophobic (*e.g.* antigraffiti) properties of the SIL/PTFE system were obtained for the compositions of a regular spherical domain pattern at the surface with the minimum surface roughness. It occurred at about 20 - 45 wt. % of PTFE content in the system. It is suggested that the regular nanopattern of F atoms of PTFE and CH<sub>3</sub> groups of crosslinked SIL component at the surface is immobilized by the semi-interpenetrating (semi-IPN) structures. The enrichment of the surface layers with immobilized F can be considered as a key factor for achieving excellent application results.

**Key words:** polysiloxane/PTFE composition, antigraffiti coatings, wettability of surface, elemental composition of surface, structure and roughness of surface.

Recently, a polymer hybrid system composed of a crosslinked polysiloxane (SIL) and a fluoropolymer (PTFE), has been developed. It has been applied as the antigraffiti and protective coatings for porous building materials [1—3].

For selecting the SIL/PTFE components their surface physicochemical properties were considered. The surface free energy (SFE) and surface roughness have been reported to be the crucial factors affecting anti-adhesion properties of coating materials [4]. Thus, the SFE of pure silicone coatings is relatively low, about 20—25 mN/m, depending on the chemical composition and on the method of coating preparation [5]. The SFE of PTFE is even lower, about 14—19 mN/m, depending on the PTFE molecular weight and also on the method of coating preparation [6, 7]. Coatings of still lower SFE,

about 10 mN/m, can be obtained by modifying polysiloxane macromolecules with fluorine-containing aliphatic side chains [8—12]. However, with side chains longer than C<sub>9</sub>, anomalies of surface properties were observed [12] due to differences in orientation of the chains. Side chains can also form a steric hindrance and limit orientation movements of polysiloxane chains that depend, in turn, on the properties of the substrate.

Therefore, to overcome the reported difficulties, semi-interpenetrating polymer network (semi-IPN) structures were prepared, in which crosslinked polysiloxane (SIL) cages could be penetrated by PTFE macromolecules. Then, physicochemical properties of such SIL/PTFE system were investigated using a multimeethod characterization of its surface and bulk properties. The following methods were applied: the tensiometry

for the determination of surface wetting properties, such as the dynamic contact angle (DCA), and for calculating SFE and its polar and disperse parts from DCA data; the x-ray photoelectron spectroscopy for chemical analysis (ESCA/XPS) to find the surface elemental composition, *i.e.*, F, C, F/C, Si, O, and in particular the Si and F atoms distributions in the surface layers; and the atomic force microscopy (AFM) to observe the surface morphology, size of domains and roughness of the surface. In the present paper, the results of recent investigations are described [13—19] and new observations are reported.

## EXPERIMENTAL

### Materials

Laboratory samples of pure SIL and PTFE components and of the SIL/PTFE system of various compositions were investigated. The SIL component was prepared from polymethylhydrogensiloxanol (PMHS) in emulsion and, after evaporation of water, it was cured in the presence of a catalyst and in the absence of PTFE. Similarly, the SIL/PTFE samples were prepared by curing PMHS in the presence of specified amount of PTFE.

The emulsions containing reactive PMHS and PTFE, as well as various non-ionic and anionic surfactants, were prepared in a laboratory Gaulin Model Lab 60/60-10TBS high-pressure homogenizer (APV Gaulin International S.A., Holland) at 6000 psi. After three runs, a stable emulsion was obtained. Before being applied the emulsion was mixed with a special catalyst in the form of an aqueous solution or emulsion. Thus, the PTFE macromolecules could be trapped into the polysiloxane cages formed in the crosslinking reactions.

PTFE component itself was in the form of an aqueous dispersion, purchased from the Tarnów S.A. Chemical Works, Poland, as a special grade of environmental-friendly solvent-free system.

Commercial samples of Antigraf<sup>®</sup>, *i.e.*, of SIL/PTFE system used as antigraffiti coatings, produced by the Chemical Plant, "Polish Silicones", Ltd., Nowa Sarzyna, Poland, were also investigated.

### Methods of physicochemical characterization

#### Tensiometry [5, 6, 13]

Samples for DCA measurements were prepared by coating of carefully washed glass cover slides with the tested emulsions and drying (curing) them at ambient temperature over 48 hours.

DCA of a liquid (water or organic solvents) on the solid tested surface was determined at 25°C by the Wilhelmy plate method, using a K12 Processor Tensiometer, (Krüss, Germany), with the K 121.2 software.

In the preliminary step, the wetted length of the pre-

pared samples was measured using n-hexane as a testing liquid. Then, the sample plates were immersed in, and withdrawn from the wetting liquid of known surface tension (water and benzyl alcohol were used). The speed of this movement was constant, the depth of immersion was 3 mm. The advancing and the receding contact angles (ACA and RCA) were calculated. The mean value of 3 measurements for each sample was taken as the result. The DCA hysteresis, *i.e.*,  $\Delta(\text{ACA} - \text{RCA})$  was also calculated to estimate the surface roughness.

SFE values were calculated from the DCA results for water and benzyl alcohol on the tested surfaces, using the Owens-Wendt equation [6] and the K 121.1 software.

#### ESCA/XPS [13, 16, 20]

Measurements were carried out in the ESCA/XPS laboratory Institute of Physical Chemistry, Polish Academy of Sciences, using the ESCALAB - 210, Fisons Instruments, VG Scientific. Samples were prepared as films on an aluminum substrate [13,16].

#### AFM [13, 16, 21—23]

Measurements were carried out in the AFM laboratory Institute of Physical Chemistry, Polish Academy of Sciences, using the TMX 2000 Discoverer SPM, TopoMetrix instrument. Samples were prepared as films on an aluminum substrate [13, 16].

## RESULTS AND DISCUSSION

### Surface properties of SIL/PTFE hybrid systems

The wettability of the SIL/PTFE surface, measured by DCA and SFE, decreases in general, as the PTFE content was increased. The increase in ACA values from *ca.* 93° for the SIL/PTFE system containing less than about 20 wt. % PTFE to *ca.* 115° for the system containing over 45 wt. % of PTFE is accompanied by the decrease in SFE values from *ca.* 17 mN/m to *ca.* 13 mN/m. Significant changes of DCA and SFE values occur from about 20 to 45 wt. % of PTFE (Fig. 1). The increase in DCA hysteresis as the PTFE content is increased indicates an increase of surface roughness. However, the hysteresis curve shows an inflexion point at a the PTFE content about 20 wt. % an a decrease in hysteresis values within the range of 20—30 wt. % of PTFE. It indicates that a minimum of roughness occurs within this range of PTFE content (Fig.1). The most significant effect is the change in the type of interactions from polar at PTFE contents below 20 wt. % to dispersive at PTFE content above 35 wt. % (Fig. 2). Thus, the ratio of SFE polar/SFE dispersive is seen to decrease rapidly within the region of 25—35 wt. % of PTFE.

The ESCA/XPS was used to determine the chemical composition of surface layers in the SIL/PTFE system at various penetration depths. Three take-off angles, *viz.*,

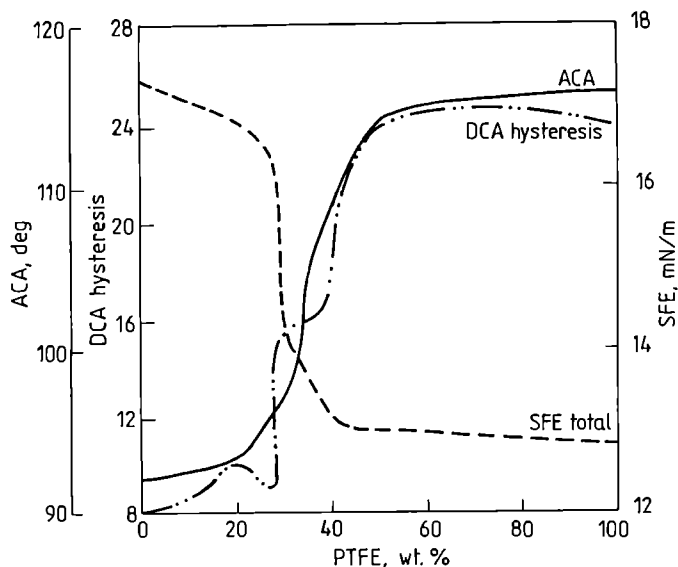


Fig. 1. Surface wettability (ACA, DCA hysteresis, total SFE), of the SIL/PTFE system in relation to PTFE content

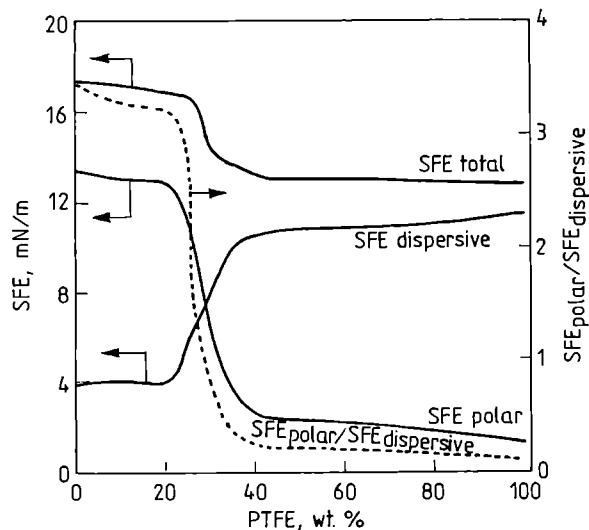


Fig. 2. SFE of the SIL/PTFE system in relation to PTFE content

10, 30, and 90°, were used with an Al — K $\alpha$  X-ray source and then the penetration depths, *viz.*, 2.1, 6.1, and 12.1 nm, respectively, were calculated for the SIL/PTFE system using the multiline method [24].

The difference between the content of F and C atoms in the surface layers and in the bulk was observed (Figs. 3, 4). The sum of F and C atoms relative to Si atoms at the surface compared with the respective values in the bulk was taken as a measure of enrichment in the hydrophobic groups at the surface layer (Fig. 3). Thus, at the depth of 2.1 nm, the surface layer is seen to have been enriched in hydrophobic F atoms and CH<sub>3</sub> groups, whereas at the depth of 6.1 nm the presence of these atoms and groups is reduced. At the depth of 12.1 nm, the (F+C)/Si ratio is similar to that in the bulk.

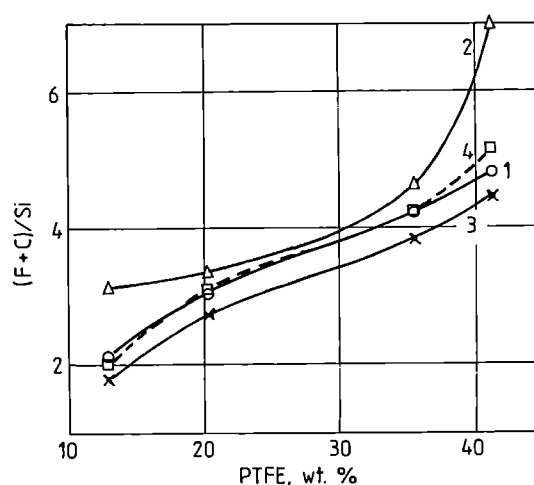


Fig. 3. The F and C atom contents in the surface layers of the SIL/PTFE system in relation to PTFE content; (F + C)/Si ratio: (1) in the bulk, calculated; measured at 2.1 nm (2), 6.1 nm (3), and 12.1 nm (4)

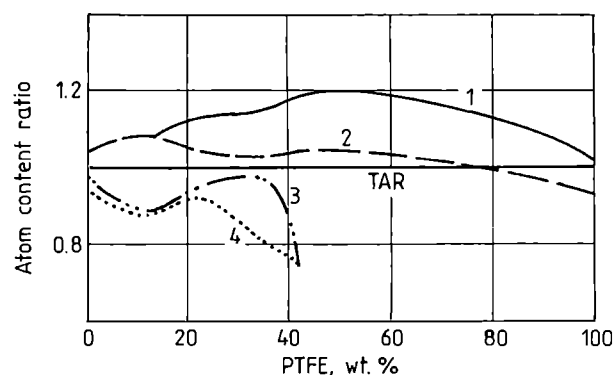


Fig. 4. The ratio of atom contents measured at 2.1 nm depth to the atom content in the bulk (subscript *t*); TAR — theoretical atomic ratio, TAR = 1; 1 — F/F<sub>*t*</sub>, 2 — C/C<sub>*t*</sub>, 3 — Si/Si<sub>*t*</sub>, 4 — O/O<sub>*t*</sub>

The ratios of the measured contents of F, C, Si and O atoms to the content of the respective atoms in the bulk (denoted by subscript *t*) are shown at the penetration depth of 2.1 nm (Fig. 4). The surface layer of pure PTFE at the depth of 2.1 nm is seen to be slightly enriched in F atoms, in accordance with the structure of the PTFE macromolecule chain in which F atoms create an “umbrella” around the carbon chain. For pure polysiloxane, the enrichment of surface layer in C atoms follows the chemical structure of the polysiloxane chain which is able to form a “brush” of the methyl groups responsible for the hydrophobic properties of silicones. In semi-IPN SIL/PTFE, the surface layer at the penetration depth of 2.1 nm is seen to be enriched in both F and C atoms (Figs. 3, 4), particularly within the range of PTFE contents about 20–60 wt. % (Fig. 4). Thus, it suggests that the surface structure is formed by the two hydrophobic constituents, *i.e.*, F atoms and CH<sub>3</sub> groups.

Quantitative analysis of surface roughness can be car-

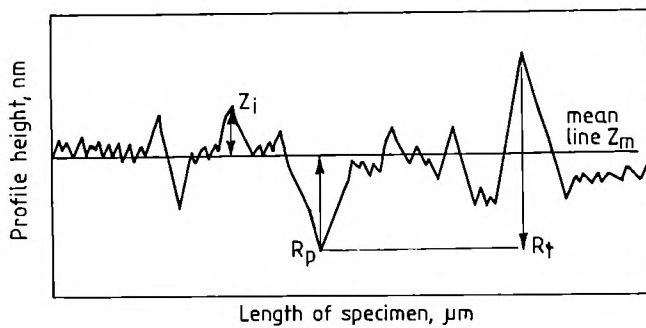


Fig. 5. Example of the SIL/PTFE surface profile

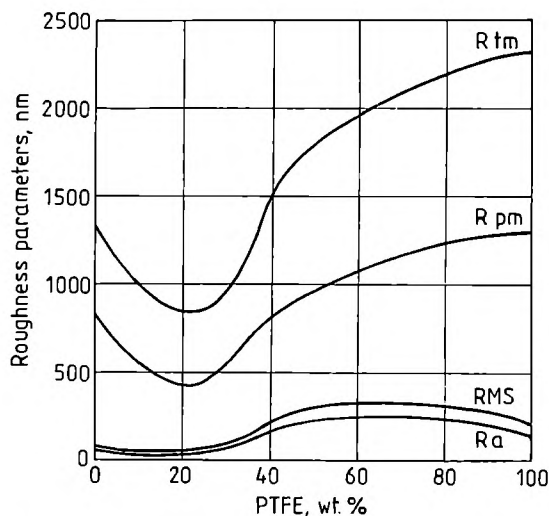


Fig. 6. Roughness parameters in relation to PTFE content:  $R_{tm}$ ,  $R_{pm}$ ,  $R_a$  and RMS (for explanation, see main text)

ried out using the AFM method and calculating the surface roughness parameters [21–23]. The most important roughness parameter is  $R_a$ , i.e., the arithmetic mean of the deviations in the height  $Z_i$  from the profile mean value  $Z_m$  (Fig. 5). The parameters  $R_p$ , i.e., the maximum height of the profile above the mean line, and  $R_t$ , i.e., the maximum peak to valley height in the profile, are also defined [22]. Considering the statistics of maximum peak heights, the mean values of  $R_p$  and  $R_t$  denoted as  $R_{pm}$  and  $R_{tm}$ , respectively, are found to be more representative of the entire profile. The other informative parameter is the root mean square (RMS) characterizing the mean values for the whole tested area of the specimen. Values of RMS roughness are calculated from the power spectral density  $P(f)$ , based on the surface line profiles  $z(x)$  at the surface, using the Fourier transform of the surface profile.

$$RMS = \left( \int_{f_1}^{f_2} P(f) df \right)^{1/2} \quad (1)$$

where  $f$  is the frequency in  $\mu m^{-1}$  for the whole specimen profile spectrum.

The effect of PTFE content on roughness parameters  $R_a$ ,  $R_{pm}$ ,  $R_{tm}$  and RMS is shown in Fig. 6. It has been found that the SIL/PTFE compositions have a very regular surface morphology with a minimum of surface roughness within the range of 20–40 wt. % of PTFE observed for each roughness parameters. This minimum is well correlated with the regular and tightly packed surface of SIL/PTFE containing about 20 wt. % of PTFE (Fig. 7).

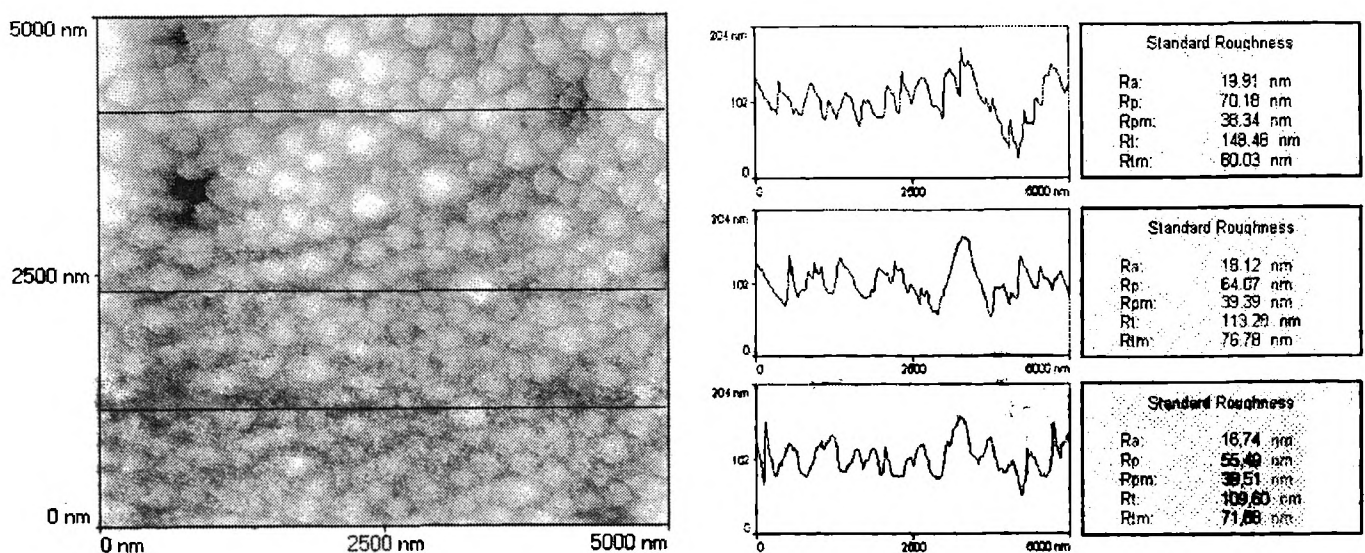


Fig. 7. The AFM micrograph of semi-IPN SIL/PTFE: (a) nanopattern; (b) surface profiles and roughness parameters

## CONCLUSIONS

Optimum hydrophobic and antisoiling (e.g. antigraffiti) properties of the SIL/PTFE system were obtained for the compositions of a regular spherical domain pattern at the surface with the minimum surface roughness. It occurred at about 20 wt. % of PTFE content in the system. It is suggested that the regular pattern of F atoms of PTFE and CH<sub>3</sub> groups of crosslinked SIL component at the surface is immobilized by the semi-IPN structures. The surface chemical composition and morphology are responsible for the low SFE and the high DCA values as well as low polar attractions observed in the semi-IPN SIL/PTFE system. The enrichment of the surface layers in F and C atoms is considered to be the key factor in achieving good application results.

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