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Morphology and thermal treatment-induced transitions in submicron films deposited from colloidal solutions of tetrafluoroethylene–acetone telomers

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An atomic force microscopy study demonstrates that thermal treatment-induced transitions in submicron films deposited on silicon, glass and mica substrates from solutions of tetrafluoroethylene–acetone telomers result from the evaporation of the solvent and short-chain telomers and reconstruction of the colloidal particle skeleton formed by higher chain telomers, the mean chain lengths of which includes 7–10 tetrafluoroethylene fragments.

Fluoro polymer coatings impart unique properties to surfaces, like a hydrophobic behaviour, antifriction, chemical and thermal stability and electric isolation.[1–3] However, submicron coatings needed for many applications are difficult to fabricate using dispersions of bulk polytetrafluoroethylene (PTFE), as well as the gas-phase polymerization of tetrafluoroethylene (TFE).[4] The method put forward earlier[5–7] utilizes the telomer solutions formed by γ-radiation-induced radical polymerization of TFE in acetone. The polymerization products are the telomers $\mathrm{Me(CF_2CF_2)_{\mathit{n}}COMe}$, where Me and COMe are fragments of acetone molecule participating in the chain radical polymerization. The chain length n depends on the initial TFE concentration c. When $c \le 0.1$ mol dm^{-3}, short-chain acetone-soluble telomers, $n \le 5$, dominated in the molecular weight distribution. The higher chain telomers become the main products at $c > 0.2$ mol dm^{-3}, when the mean chain length increases up to 7–10. In contrast to short-chain products, these telomers are insoluble and form colloidal solutions, which at the further increase in TFE concentration lead to sol–gel transition at ~0.40–0.45 mol dm^{-3}. The gelation terminates growth of the chain length by a maximum value of 10–12. Since liquid solutions are more suitable than solid gels for deposition, there exist only narrow region of TFE concentration below gelation threshold where telomer chains are sufficiently long. In accordance with the results of sedimentation rate measurements upon centrifugal separation, the mean spherical diameter of colloidal particles is ~1 μ, and the particles contain about four acetone molecules per TFE fragment on the average. Since TFE telomers are rigid rods, the suggested structure of the colloidal particles consists of a skeleton of these rods with acetone molecules embedded in this loosely shaped frame. The main peculiarity of coating deposition from the above solutions in comparison with true solutions is that the process of film formation involves, apart from evaporation of solvent and short-chain telomers, the reconstruction of the colloidal particle skeleton. The further transformation of these coatings upon thermal treatment is supposed to be also accompanied by the above skeleton degradation.

The purpose of this work was to establish a link between the colloidal particle structure and the morphology of coatings using atomic force microscopy (AFM). The measurements were performed at room temperature using the Solver NT-MDT-type equipment (Russia). Coatings were deposited on silicon, mica and glass substrates, which are characterized by a nanoscale roughness and low adhesiveness. Low adhesiveness allows for the formation of islet-type structures upon thermal treatment, in contrast to thin homogeneous layer formation on substrates with strong adhesiveness. The telomer solution (~0.05 ml) with initial concentration of TFE 0.35 mol dm^{-3} was deposited on the substrate of 1 cm^2 area. The samples after the deposition were dried up to constant weight at room temperature (typically, for a day) and then were held at the given treatment temperature for 30 min. Solution of 0.35 mol dm^{-3} satisfies the above conditions for optimal deposition: mean chain length of ~8; colloid particles occupy ~0.1 of the solution volume.

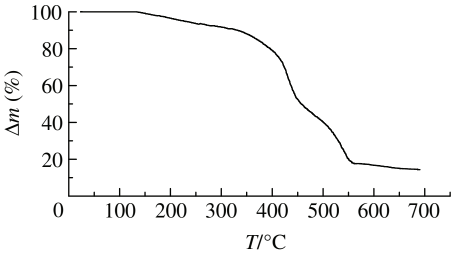

Figure 1 Thermogravimetric curve for a bulk sample of tetrafluoroethylene–acetone telomer previously dried at room temperature. Initial concentration of tetrafluoroethylene before polymerization is 0.35 mol dm^{-3}. Heating rate is 5 K min^{-1}.

The thermogravimetric (TG) curve for the bulk sample of dried telomer with the mean chain length of 7–10, deposited from the solution with the TFE concentration in the reaction mixture of 0.35 mol dm^{-3}, is shown in Figure 1. An about 20% of the mass is lost at the treatment temperatures up to 400 °C due to evaporation of acetone and short-chain telomers from the colloidal particle composition. The thermodestruction takes place above 400 °C. The destruction temperature is only by ~100 °C lower than that for bulk PTFE.[8]

The AFM scans in the amplitude and phase images on silicon and mica substrates are shown in Figures 2 and 3. The mean roughness of coatings on the area 60×60 μ amounts 304 and 228 nm on silicon and mica substrates, respectively. The above roughness corresponds to a monolayer of colloidal particles. The amplitude image of the coating on the silicon substrate

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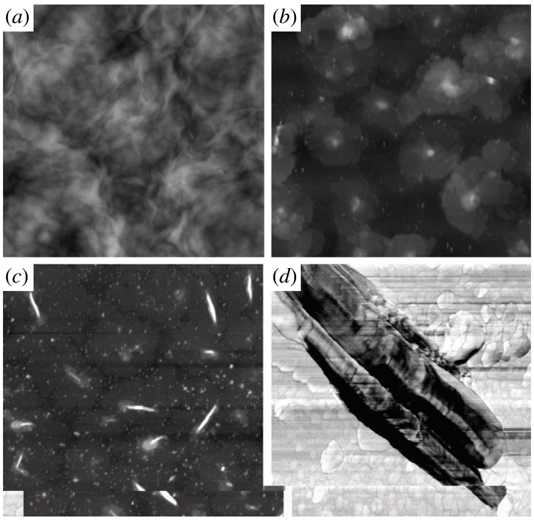

Figure 2 Atomic force-microscopy scans of coatings deposited from solution of initial concentration of tetrafluoroethylene before polymerization 0.35 mol dm^{-3} on the silicon substrate: (*a*)–(*c*) amplitude image (35×35 μ) and (*d*) phase image (2.3×2.3 μ). Treatment temperature: (*a*) 20 °C before treatment; (*b*) 160 °C; (*c*), (*d*) 250 °C.

before a temperature treatment [Figure 2(*a*)] reveals the set of globules built of micron-size blocks. After the heat treatment above 150 °C the coating morphology changes [Figure 2(*b*)]. The petal like structures coming out from the relief dense center with the diameter ~2 μ form instead of globules. At the further heating (250 °C) due to the evaporation of the low molecular fractures and melting of the other telomers, the area of petals reduces and stays the dense nanoparticles field (~100 nm) remaining on its boundary the shape of petal [Figure 2(*c*)]. The central part of structure also changes – the lengthen structures appear [Figure 2(*c*),(*d*)]. On the phase image [Figure 2(*d*)] one can see that these structures are lamela like.

The similar construction before the thermal treatment has the coatings on the glass and mica substrate. However, above 150 °C the evolutions of coating on the mica substrate differ from those on silicon substrate [Figure 3(*a*),(*b*)]. The scans measured with higher resolution demonstrates that the blocks consist of fibril-like elements, which, in turn, are formed by ensembles of oriented rods. The central part of the blocks is denser than their periphery where the fibril-like structures are shown up more clearly. Since the size scale of the blocks is the same as the mean size of colloidal particles, one can suppose that the coatings before the thermal treatment consist of micron particles modified by the partial evaporation of acetone and short-chain telomers from their composition and melting of the other telomers. The coatings preserve the above structure up to ~200 °C, when losses of the mass are near 5%. When the treatment temperature builds up, the colloidal structure becomes more pronounced [Figure 3(*a*)–(*c*)] so far as the transformations are located primarily on block boundaries. Overlapped spherical particles of 300–400 nm in diameter emerge upon the treatment at 260 °C [Figure 3(*b*),(*c*)]. The coating deposited on mica substrate exhibits clearly visible dendrite structures at the boundaries of spherical-like particles. The dendrites are constituted by chains of blocks of ~200 nm in diameter [Figure 3(*b*),(*c*)]. The isolated nanoparticles gather around the dendrites. The coating deposited on silicon substrate contains globules of the above size situated in the high density regions of the petal structures [Figure 2(*b*),(*c*)]. The treatment at 450 °C leads to the formation of islet-like structures of 200–500 nm in size [Figure 3(*d*)] when ~50% mass loss occurred, as found by TG analysis (Figure 1).

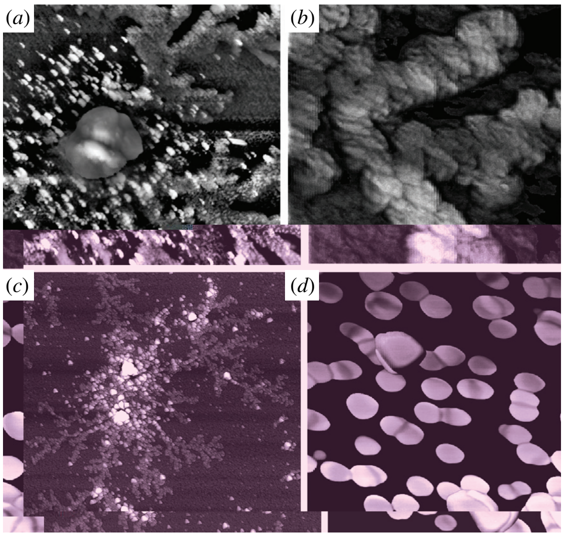

Figure 3 Atomic force-microscopy scans of coatings deposited from solution of initial concentration of tetrafluoroethylene before polymerization 0.35 mol dm^{-3} on the mica substrate: (*a*)–(*c*) amplitude image and (*d*) phase image. Treatment temperature: (*a*) 210 °C (9.5×9.5 μ); (*b*) 260 °C (2.7×2.7 μ); (*c*) 260 °C (15×15 μ); (*d*) 450 °C (2.1×2.1 μ).

The scenario of temperature-induced transformations can be suggested on the basis of AFC study. Coatings before the thermal treatment consist of the blocks, which structure is closely related to the colloidal particle structure. The colloidal particle frame is held up to treatment temperature 140 °C. The evaporation of short-chain telomers situated on the periphery of blocks leads to formation of isolated nanoparticles and dendrite structures which, in turn, include the fibrils formed by partially orientated telomers. Although the morphology of coatings varies remarkably from one substrate to another (the petal structures in combination with the plate-shape clots and the branched dendrite structures with condensed globules on the silicon and mica substrates, respectively), the common property of the coatings is the combination of globules and orientated fibrils visualized by thermal treatment at 200–300 °C. The thermal transformations result from lateral diffusion on the periphery of colloidal particles where the telomer skeleton is less stable than that in the central part. The combination of globular and dendrite elements preserves up to destruction temperature 400–450 °C when the partial destruction of telomers and evaporation of destruction products leads to the appearance of islet-like structures.

The above scenario enables us to explore the reasons of higher adhesive behaviour of telomer coatings in comparison with coating deposited from PTFE suspensions. If the size of particles exceeds the mean distance between extended surface defects (primarily, outputs of dislocations from bulk on the surface[9]), the adhesion energy per one particle is proportional to the number of surface defects which are situated on the area occupied by the particle. This number depends on the flexibility of particle elements. Since the micron-size particles of suspensions retain the lamellar structure of massive PTFE (slightly mixed rigid chains that length is of the order of particle size[8]), the number of defects coupled to each lamella is proportional to the linear density of defects in one direction. In contrast, telomers are able to couple to all defects situated on the area occupied by the colloidal particle because of high flexibility of telomer skeleton. As a result, the number of surface bonds per one TFE fragment appears to be much higher for the telomer coating than that for the suspension one.

The main result is that the colloidal solutions of the TFE–acetone telomers provide a simple method for the deposition of submicron coatings that exibit high temperature stability, which is the favourable property of fluoro-containing polymers.

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