The techniques analysis of the heterogeneous modified polymer materials parameters detection

I V Nagornova¹, F A Doronin¹, L G Varepo², G O Rytikov¹, A G Evdokimov¹, V G Nazarov¹

¹ Moscow Polytechnic University, 38 B. Semenovskya str., Moscow 107023, Russia
² Omsk State Technical University, 11, Mira av., Omsk 644050, Russia

E-mail: inagornova@mail.ru

Abstract. The comparative analysis of the most popular techniques features (SEM, EDS, XPS, FTIR) applied for the quality monitoring of the polymer materials modification process is carried out as exemplified by the both 3D-microfluidics and flexible printed electronics substrates manufacturing. The typical errors at the both microstructure and composition instrumental analysis of the modified heterogeneous near-surface layer of the polymer material are listed. The reasonability of the cyclic chemical as well as morphological statistically significant technique of the data acquisition accompanied by the source generation signal gradient variation is shown. The developed general algorithm of the polymer modification process instrumental monitoring is presented.

1. Introduction

Despite spreading SEM, EDS, XPS and FTIR techniques as the structure and composition solids analysis, some interpretation as well as the data processing problems at the analysis results matching come up frequently in context of the tool complex using, aimed to more parameters capture as the initial information for a technological process management [1, 2, 3]. More towards, the noted fact can come to the fore at the quality control of the dielectric materials manufacturing with modifiable near-surface (surface, bulk) structure [4, 5, 6, 7].

The most polymer materials (PM) with such modifiable structure are characterized as either surface or bulk heterogenous ones due to chemical, thermally and/or mechanically induced actions aimed to the attainment of the demanded operational properties. Provided that the PM structure heterogeneity, the problem of the differential charging effect state surface of the neighbouring microdomains is to appeared, potentially accompanied with the time chemical PM instability [8, 9, 10]. Consequently, it can lead to incorrect chemical analysis results interpretation as well as to the PM genuine morphology misstatements and artefact elements appearance to the same extent.

One of the significant factors affected by the decision accuracy at the modification process adjustment (running) is the mismatch of the analysis depth and modification one which can be accompanied with the modification gradient presence as well as differences in depth resolution for applied techniques complex. Whereby the most sensitive troubles can appear at the total quantitative results analysis comparison of surface near-surface and bulk PM layers in spite of the statistically significant processing.
Whereby the most sensitive troubles can appear at the total quantitative results analysis comparison of surface near-surface and bulk PM layers in spite of the statistically significant processing. So, the methodically incorrect formed basis of the primary interrelations “material parameters - modification process ones” can be misleading and, by this means cause additional investigations involvement and finally resulted in inaccurate information about operating material properties.

2. Problem statement
Some research touch on the questions of the integrated investigations methodological support in some way [3, 11, 12], but for the most researchers it is a given information based on the process physics and their own experience. Nevertheless, laboratories should have clear quality monitoring methodology at the multi-analysis control with the cause-effect relations definition, which can significantly differ depending on the research area. Thus, this study is concentrated on the technique development of comparative multi-analysis (SEM, EDS, XPS, FTIR) of both morphological and chemical parameters of the polymer substrates, which are modified at the both 3D-microfluidics and flexible printed electronics substrates manufacturing aimed to the register of the “processing parameter – criteria – analysis affected factor” relations detection and finally resulted in the process management assistance.

3. Methods and materials
In the study the results obtained by the abovementioned techniques complex is compared aimed to the characterization of PET polymer substrates modified by multiphase fluorination method according to [13] with variable processing parameters provided the substrate operating properties performance in terms of their geometry (roughness) and surface energy [13, 14]. The both initial and modified PM morphology characterization was carried out using FE-SEM (JSM-7500F) at variable modes, accelerating voltages (AV, from 0.3 to 20kV) and probe current; the samples were pre-coated by Pt layer (about 10nm) to avoid strong surface charging. Element and chemical analysis results were accumulated by EDS (Oxford X-Max80, INCA, AVmin 5 kV), ATR-FTIR (FT-801, the analysis depth 10-20 µm), MATR-FRIR (FSM-120, the analysis depth 5-10 µm based on ZnS crystal) and XPS (JPS 9200, in presence of the charge neutralisation procedure). The both x-ray generation and beam electron penetration area calculation was realized by Casino v2.48 software.

4. Results
Based on the earlier study [13] the table of correlation between monitoring parameter and affected analysis factors at the modification process was formed (table 1).

As it clear from the table 1 one of the most critical factors for the comparative quantitative analysis procedure (in terms of d, M, KSm) is the analysis depth, which value seriously is varying within the only technique as it exemplified by SEM - depending on the analysis mode, material density, as well as between methods based on different physical principles of the signal source and material interaction. The known informative way of the rough errors elimination at the results interpretation is the signal generation area Monte-Carlo simulation [14, 15]. The simulation accuracy is defined by a lot of input factors, including the equipment parameters, the calculation model, material formulas, etc. The method gives an idea of an average area of the signal generation at the demanded observation condition (figure 1, figure 5 - the technique is involved in Block A of the developed algorithm as the most critical stage).
Table 1. The monitoring parameter - affected analysis factors correlation.

| Parameter                          | Symbol, measuring unit | Analysis technique | Affected analysis factors |
|------------------------------------|-------------------------|--------------------|---------------------------|
| 1 Modification depth / inaccuracy  | d, nm $\Delta d$       | SEM, EDS, IR*      | Analysis depth            |
|                                    |                         |                    | Depth resolution          |
|                                    |                         |                    | Spatial resolution        |
|                                    |                         |                    | Analysis time             |
| 2 Modification degree             | M, %                    | EDS, XPS, MATR-FTIR, ATR-FTIR$^3$ | Analysis depth |
|                                    |                         |                    | Analysis time             |
| 3 Modified elements area per the sample area unit | $K_{Sm}$, % | SEM, EDS | Spatial resolution |
|                                    |                         |                    | Analysis time             |
| 4 Modified layer thickness / inaccuracy | $b, nm/\Delta b$ | SEM, EDS | Analysis depth |
|                                    |                         |                    | Depth resolution          |
|                                    |                         |                    | Spatial resolution        |
| 5 Defect number per the sample area unit | $N$, each | SEM | Analysis depth |
|                                    |                         |                    | Depth resolution          |
|                                    |                         |                    | Spatial resolution        |
| 6 Stability over time             | $M_t$, hours            | XPS                | Time                      |

Figure 1. The example of the both x-ray generation and beam electron penetration area visualisation (into PET bulk, presented inside red square) at the acceleration voltage increasing calculated by Monte-Carlo method.
The practical and effective method of both the modified layer(s) and the discrete modified areas localization (spatial and bulk) as well as their thickness (b) control is parallel SEM-EDS analysis of material surface and cross section (figure 2a-d) by tracing so-called indicator elements (figure 2d) of the modifiable active components. The technique is adequate at the condition of material structure permanence providing at the cutting procedure.

The most sensitive problem of the abovementioned techniques application is averaging and quantitative superposition of the data from the neighbouring analyzing microdomains, especially in case of their inadequate areas (bulk) (figure 2c) resulted in inaccurate estimation of the modification degree (M) as well as the modified domain size ($K_{Sm}$) due to drastic difference in the SEM and EDS spatial resolution (some order) at the secondary (backscattered) electrons or characteristic x-ray generation. Additionally, provided the fact that the higher AV, the grater PM destruction risqué as well as the morphology changing due to the local thermal heating (figure 2c), an opportunity of cyclic analysis application of the same domains aimed to the time stability testing ($M_t$) is excluded. Moreover, the information about genuine defectiveness value (N) can be mispresented.

With full clarity of analysis depth verification necessity at the comparative analysis, there is the question of modification inhomogeneity (both spatial and bulk) effect on the quantitative data (figure 2a, c). Thus, the information about quantity of the indicator elements in case of their proved presence, but localization within the low thickness layers (b is less than calculated generation area dimension) or domain size can pass to the instrumental uncertainty.

Under the condition of low EDS informativeness (similar to the pointed cases) whereas identification of clear morphological markers changing, as well as the next characterization method, the techniques for material modification proving can serve various type of IR-spectroscopy (figure 3) and XPS-analysis (figure 4) [16]. The last one can be extended due to standard procedure of layer-by-layer ion etching.

It should be stressed that listed techniques sequentially add each other being the base for the next conclusions: SEM information about the discrete modification is accompanied with the morphology thermal variation problem detection (figure 2); the EDS data determinate the localized indicator element traces, but total quantity is averaging from the full x-rays signals generation area; listed results are summarized with the IR-information (figure 3) about the
Figure 3. IR-spectrums of the initial and fluorinated PET collected from different depth.

Figure 4. The example of C 1s and F 1s XPS-spectrums variations of fluorinated PET after the cyclic acquisitions procedure.

functional groups presence with depth grading possibility; finally, cyclic accumulated XPS-spectrums show chemical state time-variability (figure 4) without any outside actions.

Herein, but for the accumulated data information about the spatial and bulk discretization of modification layers (domains), the both IR and XPS spectrums would not correlate even in case of their shape stabilization. Despite XPS spectrums time-variating, the in situ cumulated information can be useful as data about the chemical PM surface transformation. Thus, the cyclic monitoring of the chemical state in parallel with morphological control the analogue areas is the effective method of modification parameters determination.

So, in figures 2 - 4 the approach example of the PET surface modification monitoring is presented which was transformed to the general algorithm of the PM modification process instrumental monitoring (figure 5).

Conclusion
The presented comparative analysis algorithm developed for modification process characterization of the polymer material with heterogenous near-surface layers allows to increase the monitoring validity. The novelty and practical relevance of the approach consist of modification
Figure 5. The general algorithm of the modification process instrumental monitoring. The following terms are used: IPM – initial polymer material; MPM – modified polymer material; AV – accelerating voltage; IE -indicator element. We suggest both the sample preparation procedures and analysis adjustment are performed correctly.
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