ISSN 1560-8034, 1605-6582 (On-line), SPQEO, 2019. V. 22, N 4. P. 470-478.

On the importance of interface interactions in core-shell nanocomposites of intrinsically conducting polymers

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Abstract. In this mini-review, we address the importance of specific interactions in core-shell structures composed with intrinsically conducting polymers (ICPs) as a shell and various nanoparticles used as a core. These interactions that can appear during the polymerization process of corresponding monomers or in the course of subsequent treatments of already formed core-shell nanocomposites play a crucial role in determining their structure and unique physical properties. They also lead to significant differences in molecular weight, structure, oxidation state, electronic properties, thermal stability and other properties of synthesized ICP shells in comparison to their pure state when polymerization proceeds without a template. This work was reported on the joint Ukrainian-Japan workshop in the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine on 23rd December 2018.

Keywords: intrinsically conducting polymers, (nano)composites, core-shell, interactions, molecular characteristics, structure, morphology, properties.

https://doi.org/10.15407/spqeo22.04.470
PACS 81.07.-b, 78.67.Bf, 78.67.Sc

Manuscript received 12.07.19; revised version received 26.07.19; accepted for publication 29.10.19; published online 08.11.19.

1. Introduction

Since the first publication by Shirakawa, MacDiarmid, Heeger *et al.* [1], which introduced intrinsically conducting polymers (ICP) to scientific community 41 years ago (followed by awarding the Nobel Prize in Chemistry in 2000), the field of these interesting polymers has developed in a broad diversity of novel applications including computer displays, light-emitting diodes, solar cells and field-effect transistors, materials for EMI shielding, antistatic and anti-corrosion protection, batteries, catalysis and electrocatalysis, sensing and membrane systems, biomedical and bioelectronic devices and many others [2-6]. One can confidently assert that these interesting polymers are among the most successful and important discoveries in modern polymer physics, chemistry and material science. Due to the presence of long conjugated chains in their structure, these polymers in most cases are photosensitive, exhibit semiconducting properties and are capable of participating in charge generation processes, when being photoexcited and, moreover, can be *p*-doped and, in some cases, *n*-doped.

However, ICPs are not free of serious drawbacks, namely: brittleness, infusibility and insolubility, which cause their poor processibility and hinder some practical applications. These problems can be bypassed through development of composites and nanocomposites; application of special dopants; functionalization of the monomer or polymer fractions, as well as via synthesis of nanoparticles of conducting polymers [7]. Naturally, each of these approaches has advantages and disadvantages and can be chosen depending on the task that should be solved. Sometimes, a simultaneous use of all or part of the approaches can be the most effective, especially in the case of preparation of ICP (nano)composites. In particular, these materials can be prepared by mixing ICP with another component or by polymerization of the corresponding monomer (aniline, thiophene, pyrrole or their derivatives) in the presence of another component [7-9]. If in the first approach synergism of the physical properties can be observed only in limited cases, in the second approach it prevails due to formation of intimate contacts and specific interactions between all participants of the polymerization process. Obviously, this specificity is most noticeable in the case of nanocomposites or

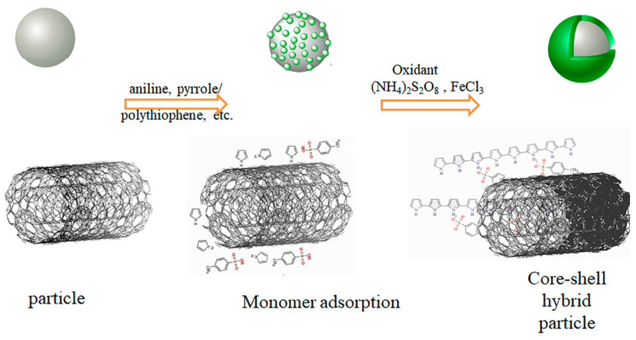

Fig. 1. Scheme of formation of (nano)composites with core-shell morphology, in which the core has polymeric or inorganic nature, and the shell is the ICP layer deposited on the surface of the nanoparticle due to polymerization of the corresponding monomer under the action of an oxidant.

composites with core-shell morphology, in which the core has polymeric or inorganic nature, and the shell is the ICP layer up to several tens of nanometers thick, deposited on the surface of the nanoparticle due to polymerization of the corresponding monomer under the action of an oxidant (Fig. 1).

In general, polymerization proceeds through two main steps: 1) adsorption of the monomer on the surface of nanoparticles dispersed in the reaction medium, and 2) its activation under the action of a suitable oxidant [7-10]. This process is completed with formation of hybrid particles with the ICP shell and core composed by another component. Formation of this morphology and its dependence on interactions between the components in hybrid (nano)particles was confirmed for various shells: polyaniline (PANI), polypyrrole (PPy), poly(3-mehylthiophene) (P3MT) as well as cores of different size and origin (poly(vinylidene fluoride) (PVDF), polycarbonate (PC), poly(vinyl chloride), Fe_3O_4 and SnO_2, TiO_2 rutile and anatase, multiwalled carbon nanotubes (MWCNT), *etc.*) [10-33]. Undoubtedly, a precise control of specific interactions between the components during the polymerization process is a key issue offering additional possibilities in creating new materials of this type. Such control allows a directed synthesis of the ICP shell with predetermined structure, morphology and desired properties.

2. Physical-chemical aspects of the nanocomposites formation

In order to find a way to realize such control, we monitored changes of the open circuit potential (OCP) and pH of the reaction media in the course of oxidative polymerization of aniline and heterocyclic monomers in absence and presence of other components. This approach enabled tracking changes in oxidation states of the conducting polymers forming the shells at the surface of the matrix (template) components [10-12]. Specifically, OCP and pH profiles for aniline polymerization can reveal characteristic time points corresponding to the most important stages of this process. In the case of titania and MWCNT core materials, this formed a basis for estimation of kinetic parameters inherent to the polymerization process [13, 14]. In particular, in Fig. 2 one can observe a characteristic induction period (t_{ind}). At the next stage, an increase of the potential in the OCP profile indicates appearance of pernigraniline oligomers (point t_{PN}) and then of insoluble pernigraniline phase at the end of the second stage. Pernigraniline is the most oxidized state of polyaniline, which catalyzes at the third stage further polymerization process of aniline and accelerates the growth of the potential. Approximately at the midpoint of the third stage, partial reduction of the growing pernigraniline chains by the monomer takes place leading to appearance of emeraldine units. As a consequence, the potential growth slows down; it reaches a maximum (t_{max}) corresponding to the final content of pernigraniline and to the exhaustion of the oxidant in the polymerization mixture. Then, the pernigraniline phase is reduced by the monomer residues (t_{red}), and the potential drops (t_{ES}) to a value reflecting the amount of polyaniline formed in its most stable form of emeraldine salt (Fig. 2). All these stages are accelerated in the presence of dispersed nanoparticles. An important practical result of this study is that the reciprocal values of durations of these stages depend linearly on the content of the dispersed phase [13, 14].

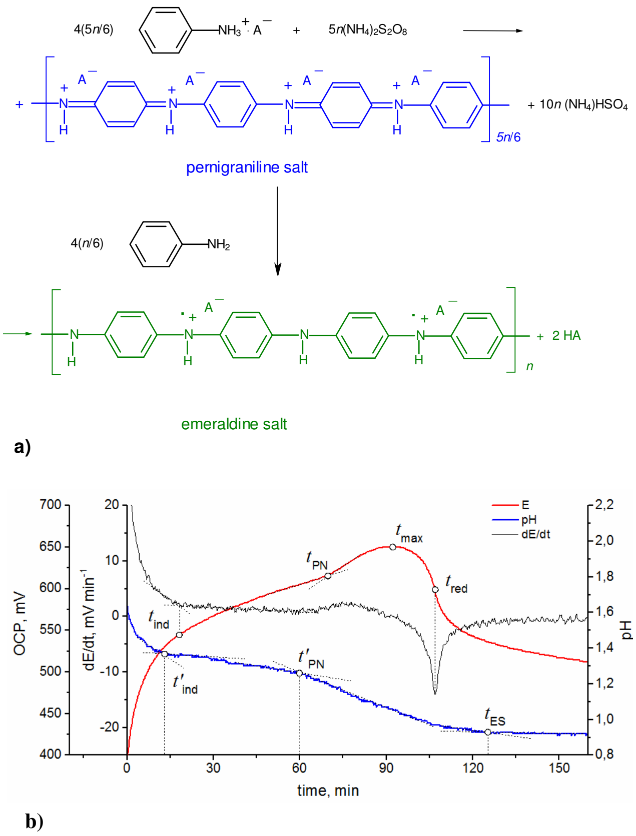

Fig. 2. Scheme of formation of different oxidation states of polyaniline during the polymerization (a) and OCP (*upper curve*), pH (*bottom curve*) and its first derivative (*middle curve*) profiles for polymerization in the presence of TiO_2 (TiO_2/An weight ratio = 80:20) [10, 11, 14].

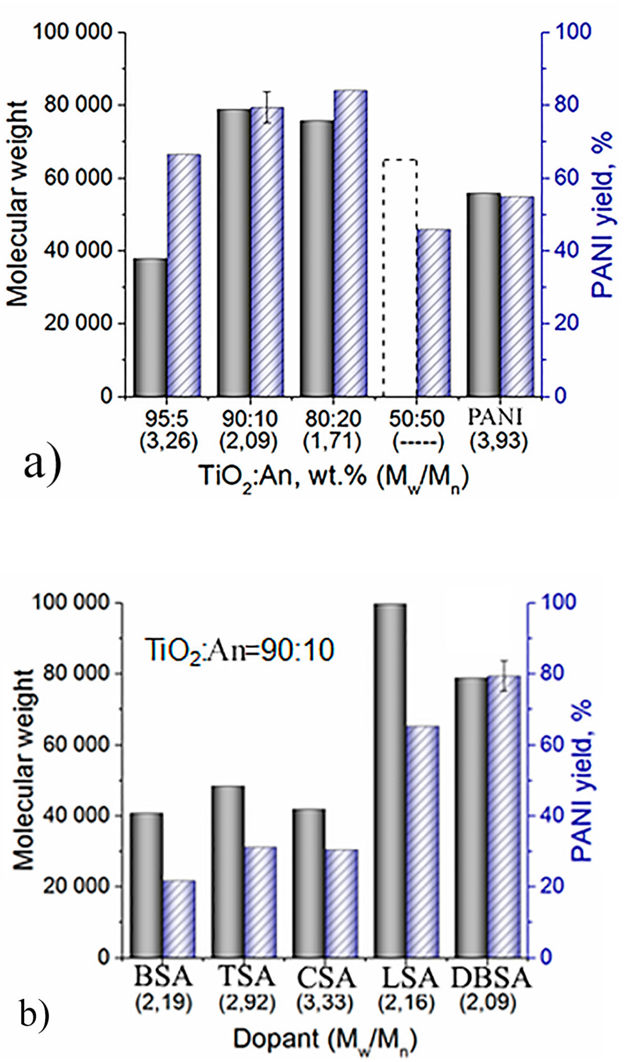

Fig. 3. The nanoparticles (a) and acid-dopant (b) influence on PANI molecular weight and yield.

The presence of dispersed nanoparticles and various acids-dopants in the reaction medium not only significantly affect the kinetics of the aniline polymerization [10, 13, 14], but also determines the molecular characteristics and yield of the polyaniline product [14]. In particular, titania nanoparticles increase the molecular weight and yield of polyaniline by about 40% (Fig. 3a).

At the same time, polyaniline obtained in the presence of “large” surface-active lauryl sulfate acid (LSA) and dodecylbenzenesulfonic acid (DBSA) was characterized by about 2 times higher molecular weight and polymer yield as compared to the case of using the acids without surface activity (Fig. 3b). Apparently, this may be due to the fact that surface-active acids form micelles in solution, which absorb the monomer and, probably, nanoparticles, thus creating the effect of a micro-reactor with an increased concentration of participants [12, 14].

3. Structure-property relationship of the nanocomposites

Molecular level changes in the polymer shell of the nanocomposite particles are inevitably accompanied by changes in the structure, morphology, charge states, conductivity, sensing activity and other properties of both the shell itself and nanocomposites as a whole. For example, it was found that P3MT-Cl synthesized in the absence and presence of PVDF submicron (200 nm) particles revealed strong morphological, structural and spectral differences [31]. Specifically, one can distinguish three levels hierarchical morphology of pure P3MT-Cl in the TEM and SEM images (Fig. 4).

The first level is presented in this TEM image by flake-like primary nanoparticles of sizes 20–60 nm. At the second level, these particles form aggregates of a few hundred nanometers. SEM image reveals the third level in the hierarchy, which involves P3MT-Cl nanoparticles in agglomerates from 2 up to 8 μm. By contrast, the P3MT-Cl in the composite shows only one level of organization represented by nanoparticles arranged in irregular shells surrounding the PVDF particles. Moreover, the size 20–40 nm and polydispersity of the nanoparticles of the P3MT-Cl phase are slightly lower than that of the pure P3MT-Cl particles.

An impressive difference in morphology and the aggregation hierarchy of P3MT in the composite as compared to the same polymer in its pure state could be confirmed by photoluminescence (PL) spectra of dedoped samples. In particular, in the case of concentrated dispersion (0.5 mg/ml) in acetonitrile of the pure P3MTr (0.5 mg/ml, Fig. 5, curve *1*) the observed emission peak revealed a vibronic structure with two maxima and several shoulders on the both sides [31].

This peak was decreased and blue-shifted after dilution of the dispersion (curve *2*). Moreover, a new PL peak appeared in the vicinity of 525 nm. The subsequent settling of this diluted dispersion for 2 hours was accompanied by dropping of the total emission intensity and by an additional blue shift of this maximum (curve *3*). Furthermore, after sedimentation of the dispersion for the following 48 hours, the P3MTr emission above 600 nm strongly dropped, while the 525 nm peak remained at practically the same level and was similar to the nanocomposite one (Fig. 5, curve *4*) [31].

Based on the TEM and SEM images of the samples (Fig. 4), these changes in the emission due to dilution and sedimentation were interpreted as a manifestation of the influence of the size of the hierarchically arranged P3MT nanoparticles on their emission properties [31]. These results suggest that the low-energy maximum at 685 nm can be assigned, at least partially, to the largest agglomerates of the P3MTr particles. This assignment is supported by the coincidence of the PL spectra of the concentrated dispersion (Fig. 5, curve *1*) and the P3TMr film prepared from this dispersion. In line with this suggestion, one can assume that the PL spectra of the diluted and 2 hours settled P3MTr dispersions (curves *2* and *3*) above 600 nm display emissions of aggregates with intermediate sizes, while the individual (non-aggregated) nanoparticles of the pure P3MTr emit at higher energies

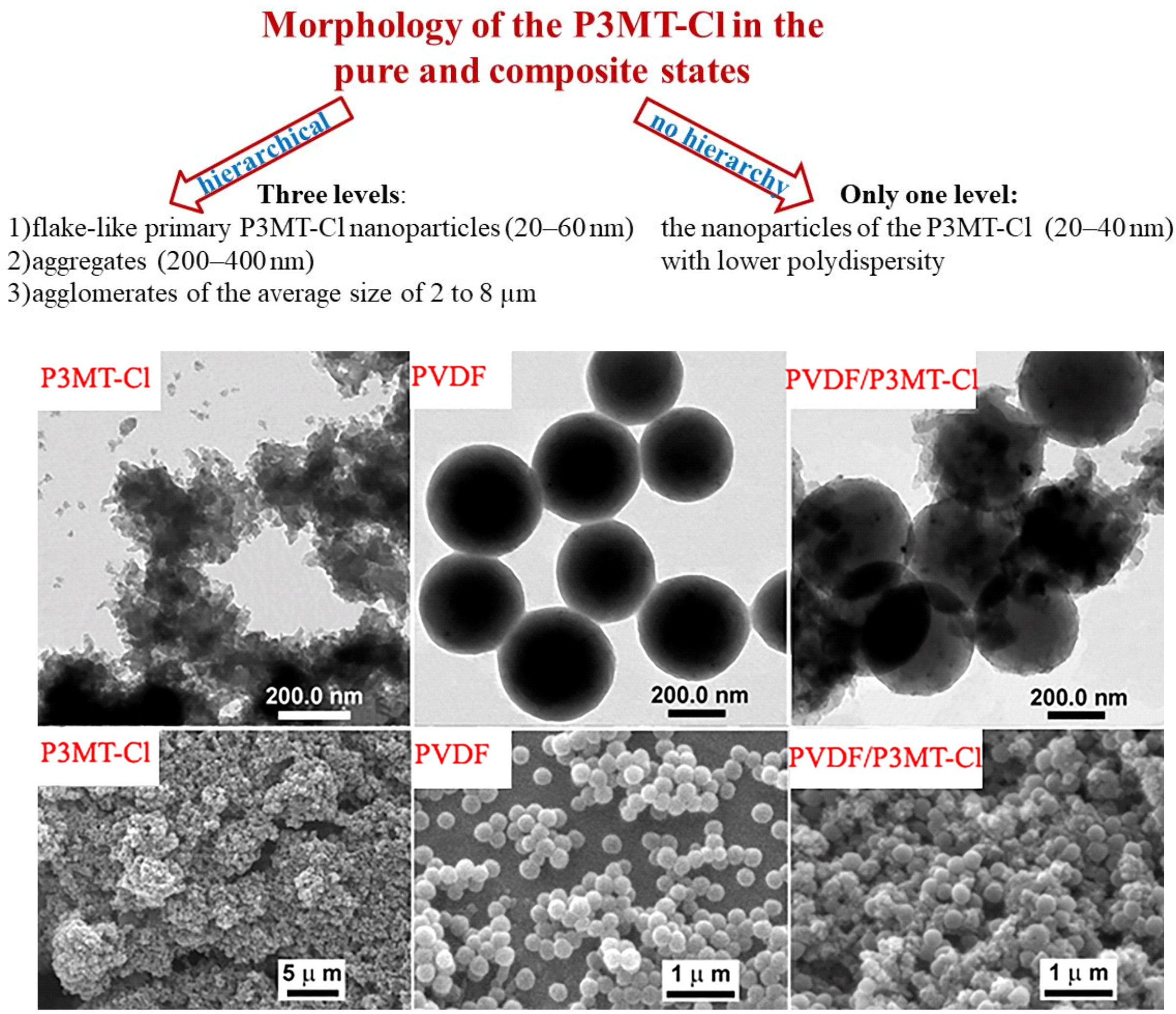

Fig. 4. TEM (top row) and SEM (bottom row) illustrations of the morphological specificity of pure P3MT-Cl and PVDF/P3MT-Cl core-shell nanocomposite. Adapted from [31].

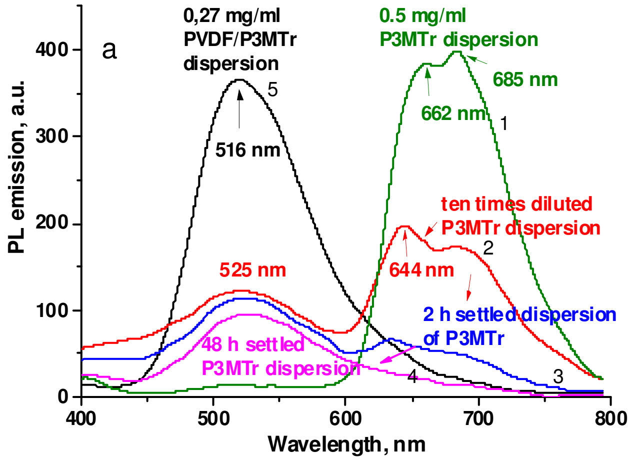

Fig. 5. Photoluminescence spectra of the reduced P3MT (P3MTr) dispersion in acetonitrile (*1*), (*2*) ten-fold diluted pure P3MTr dispersion, (*3*) diluted pure P3MTr dispersion after 2 hours of sedimentation, (*4*) diluted pure P3MTr dispersion after 48-hour sedimentation, (*5*) PVDF/P3MTr dispersion. Adapted from [31].

with the peak at about 525 nm. The latter peak became the only observed peak after 48 hours of sedimentation of the P3MTr dispersion (curve *4*).

Moreover, and even more important, this peak is similar to the peak of the composite located at about 516 nm (curve *5*). The blue shift of this PL peak of the composite, as compared to that of the pure P3MTr, agrees with different state of the P3MT nanoparticles in the composite shells. It should be emphasized here that the vibronic structure of the PL peak both of the pure and composite P3MTr confirms the above discussed ordering of the P3MTr fractions. The observed ordered phases appeared probably due to π–π-stacking interactions between P3MT's backbones and formation of molecular aggregates typical for P3ATs [31].

Structure differences between the conducting polymer in pure and composite states were confirmed for different (nano)composites [16, 17, 19, 23, 25, 26, 29, 30-33]. For example, from the XRD-spectra of doped polyaniline and its nanostructured composite with polycarbonate (PC), we found that its degree of crystallinity in the pure state was about 3 times lower, and

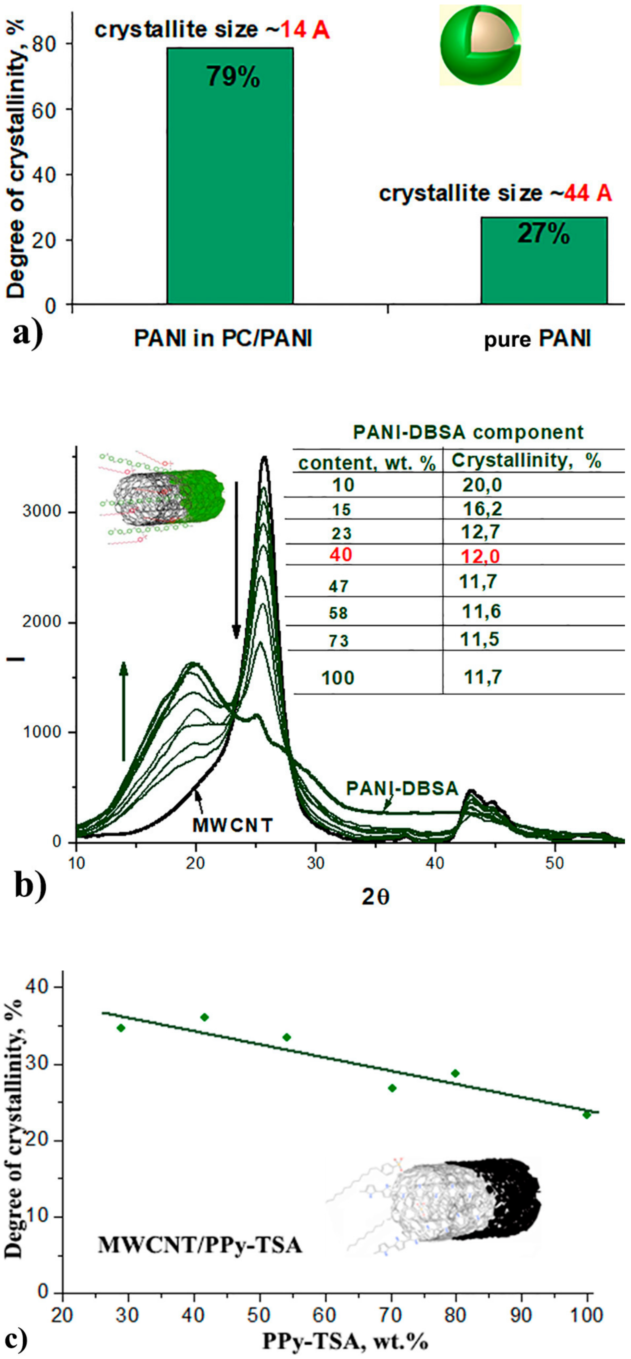

Fig. 6. XRD evidences of the structure differences between the conducting polymers in pure and composite states (core-shell composites): a) the degree of crystallinity and size of crystallites of the doped PANI in pure state and in the shells on the surface of the PC particles (adapted from [25]); the crystallinity changes in doped PANI (b) or PPy (c) phases in nanocomposites with MWCNT (adapted from [29, 35]).

the average crystallite size was 3 times higher than that in the composite (Fig. 6a) [25]. Moreover, in the case of nanocomposites of carbon nanotubes with polyaniline (Fig. 6b) and also polypyrrole (Fig. 6b) an increased crystallinity of ICP in the nanocomposite, especially at its low contents, was observed [29, 35].

It is obvious that, similarly to molecular characteristics, these differences in the structure of conducting polymers in the shells are the result of specific interactions between the components of the nanocomposite. In particular, it was proved that amino groups of PANI in the shells formed hydrogen bonds with PC [25] or PVDF matrix (core) components in the case of the PVDF/PANI and PC/PANI nanocomposites. It was confirmed by the shifts of vibrations of H-bonded N–H groups of polyaniline in pure and composite states, as well as by the shifts of vibrations of C–F and C=O bonds in the matrix polymers, respectively.

Interactions of ICP in the shell with the matrix component also lead to a change in its oxidation state. Specifically, it was found from Raman spectra of PC/PANI composites that the number of quinonoid units in PANI, reflecting its oxidation level, is noticeably lower in the composite than in the pure state [25]. This variation in the PANI oxidation level inevitably affected its electronic structure. Consequently, the calculated number of polarons was smaller, and the number of bipolarons was higher for the pure PANI as compared to the PANI phase in the composite [25].

Based on the higher mobility of polarons as charge carriers in PANI, we assume that conductivity of the doped PANI phase in the composite can be higher than that of the pure doped PANI. Indeed, it was found for the cold-pressed pellets of PC/PANI composites that conductivity of the pure PANI doped by toluene sulfonic acid (TSA) was about three times lower than conductivity of the PANI-TSA composite phase in a composite with polycarbonate [25]. In the case of the titania nanocomposite, the phase of PANI doped by dodecylbenzenesulfonic acid (DBSA) also had higher conductivity than pure PANI-DBSA [28] (Table).

The data for PANI (nano)composites [25, 28] were confirmed for other ICP based materials. For example, according to Raman spectra of poly (3-methylthiophene) (P3MT) and its nanocomposite with PVDF [31], one can estimate that the number of charge carriers, *i.e.* polarons and bipolarons, are, respectively, 25 and 35% higher in the pure P3MT-Cl as compared with the P3MT-Cl located in the nanocomposite shell. This, in general, indicates a lower doping and conductivity of the composite P3MT-Cl phase.

Obviously, this specificity of ICP nanocomposites at the molecular level affects their practically important macro-properties, too. In particular, as one can see from thermograms of the pure doped P3MT-Cl and dedoped P3MTr as well as their nanocomposites with PVDF, thermal stability of P3MT (doped or dedoped one) is lower as compared to its nanocomposites (Fig. 7a) [31].

The initial temperatures of thermal degradation of the phases of doped P3MT-Cl and dedoped P3MTr in nanocomposites are shifted toward higher temperatures by about 20 and 40 °C as compared to the pure nanocomposite and specific interactions of P3MT and polymers. Although the mechanism of these changes is not clear yet, according to the said earlier they may indicate that the increase in the thermal stability of P3MT is caused by both its specific properties in the PVDF.

Table. PANI conductivity in the pure and (nano)composite states.

Sample	σ_0, S/cm	Method of preparation
Pure PANI-TSA	1.6	Cold pressed pellets [25]
PC/PANI-TSA	5.2	Cold pressed pellets [25]
PC/PANI-TSA	0.1	Compression molded (at 240 °C) films [25]
Pure PANI-DBSA	0.4	Cold pressed pellets [28]
TiO_2/PANI-DBSA	0.6	Cold pressed pellets [28]

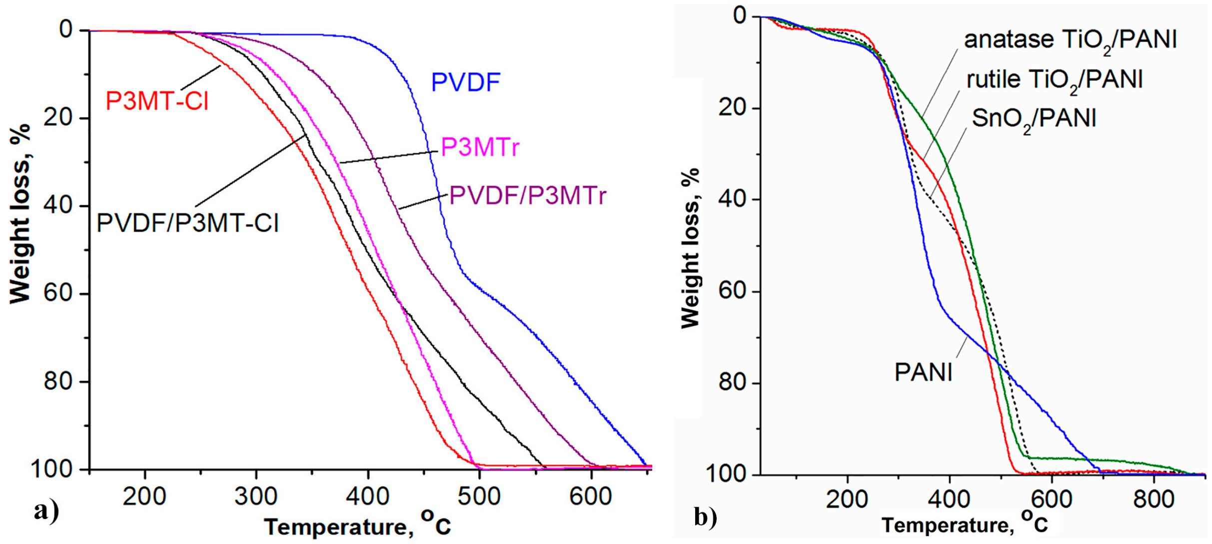

Fig. 7. Thermograms of PVDF/P3MT (a) (adapted from [31]) and $TiO_2(SnO_2)$/PANI-DBSA nanocomposites (b).

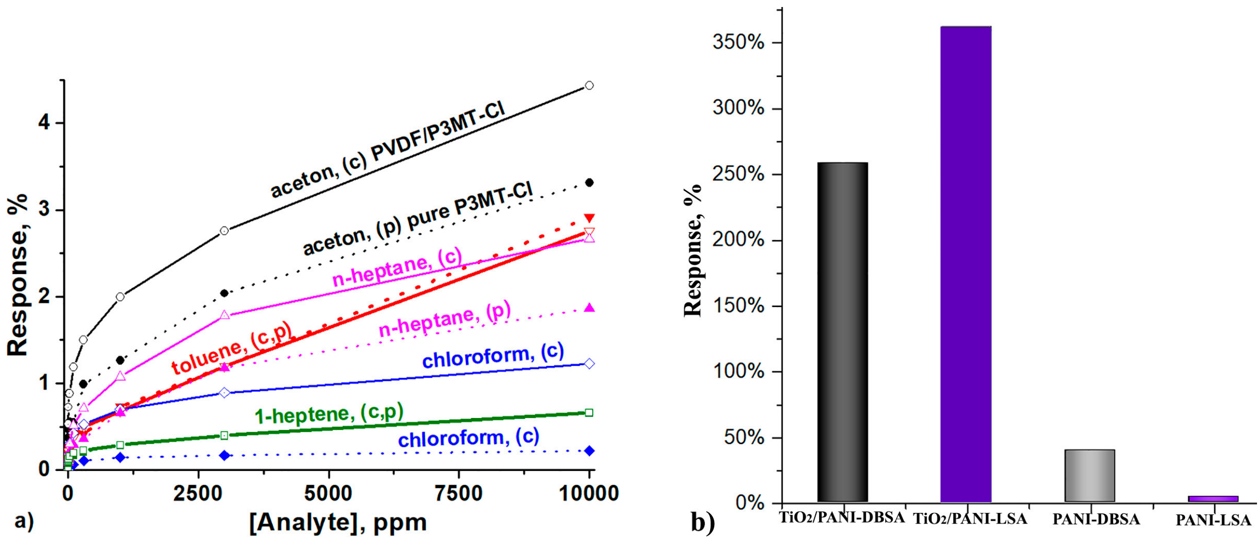

Fig. 8. a) Calibration curves of the sensor responses of the pure P3MT-Cl (p) and PVDF/P3MT-Cl nanocomposite (c), adapted from [31]; b) response magnitudes comparison of the TiO_2/PANI-dopant nanocomposites and pure PANI-dopant synthesized materials at 10 ppm of ammonia, adapted from [26].

This conclusion agrees with the influence of the nature of oxide nanoparticles on the thermal stability of their stability nanocomposites with PANI. In particular, one can see in their thermograms within the range 280…450 °C that weight losses decrease in the row: tin oxide > rutile > anatase (Fig. 7a).

A striking confirmation of the improved molecular characteristics of conducting polymers in core-shell composites is their sensing properties. Specifically, as one can see in Fig. 8 the sensor responses of the PVDF/P3MT-Cl (c) nanocomposite are stronger in cases of acetone, chloroform and n-heptane than those of the pure P3MT-Cl (p) [31]. However, the responses of the nanocomposite and pure P3MT-Cl to vapors of unsaturated hydrocarbons (toluene and 1-heptene) are almost the same. Such influence of the nature of the analyte on the sensor responses of the materials was assigned to the relationship between the work function of P3MT-Cl and electronegativity of the analyte [31].

Synergistic enhancement of sensor responses was also observed in the case of hybrid core–shell nanocomposites of other conducting polymers – PANI and PPy. A particularly strong effect is achieved for titania and PANI nanocomposites, in which the response to ammonia exceeds that of pure PANI by ~ 7 times (in the case of the dopant DBSA) and ~ 90 times (in the case of the dopant LSA). This strong effect can be associated not only with the specific properties of the polyaniline shell in the nanocomposite, but also with formation of a *p-n* junction between polyaniline and TiO_2.

4. Conclusions

Concluding this brief review, we would like to emphasize the importance of specific interactions between components of the nanocomposites with core-shell morphology, in which the core is overcoated with the ICP shell (or nanolayer) deposited by polymerization of the corresponding monomer. Finding the ways to control these interfacial interactions will open significant perspectives in creating new multifunctional (nano)-composite materials with specified properties. It is clear that the effectiveness of such control depends not only on the choice of the core and shell materials, but also to higher extent on variation of the structure and properties in the polymer shell associated with both conditions of its formation and a vicinity of the core substrate. Therefore, clear understanding of peculiarities of structural organization of ICP in the shell and interfacial interactions responsible for these peculiarities are crucially important and should be a subject for further studies in the field.

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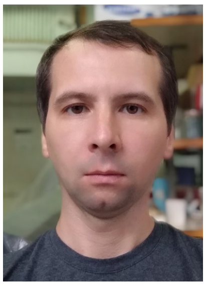

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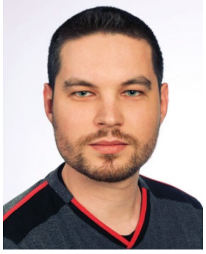

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