Optical measurements of electrophoretic suspension kinetics

V. Siderov[1], R. Yordanov[2], I. Yordanova[2], S. Boyadjiev[3], M. Vala[1], V. Milenkov[1], P. Heinrichova[1], M. Weiter[1], and I. Zhivkov[1,4*]

[1]Brno University of Technology, Faculty of Chemistry, Centre for Materials Research, Purkynova 118, 612 00 Brno, Czech Republic

[2] Technical University - Sofia, Faculty of Electronic Engineering and Technologies, Department of Electronics, 8 Kliment Ohridski blvd., 1000 Sofia, Bulgaria

[3]Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, Technical Analytical Chemistry Research Group of the Hungarian Academy of Sciences, H-1111 Budapest, Muegyetem rakpart 4., Hungary

[4]Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev Str. bl. 101/109, 1113 Sofia, Bulgaria

Electrophoretic deposition (EPD) was originally used for formation of coatings, e. g. in the automotive industry. Recently EPD is successfully utilized for thin film preparation with an application in the optics and electronics. This paper investigates the process of the suspension formation and aggregation by ultraviolet and visible spectroscopy (UV-VIS) spectroscopy and Dynamic Light Scattering (DLS) methods. The suspensions were formed by a precipitation of solution of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] in toluene using acetonitrile as a precipitator. It could be concluded that the progressive suspension particle growth observed by DLS affects regularly the first derivative of the UV-VIS spectra. By a comparison of the results obtained by both methods it could be seen that UV-VIS spectroscopy combined with the spline method could be successfully used for an estimation of electrophoretic suspensions.

Keywords: Electrophoretic suspension characterization, UV-VIS spectroscopy, Dynamic light scattering, Kinetics of suspension particle growth.

INTRODUCTION

In the recent years the electrophoretic deposition (EPD) is successfully used for a thin organic film preparation for the purpose of the organic electronics. The method allows casting films of several hundred nanometers from low suspension concentration. The particle size in the EPD suspension could be controlled by changing the ratio of solvent and non-solvent [1] without using surfactant additives [2]. EPD potentially enables quick patterned deposition, because the deposition area can be specified by the electrification of selected electrodes [3].

Ultraviolet and visible spectroscopy (UV-VIS) measurements are often used for electrophoretic suspension characterization. The material efficiency of electrophoretic deposition of a fluorene-based conjugated polymer, from suspensions with a mixture of acetonitrile and toluene as dispersant was studied by taking a snapshot of the material concentration by measuring absorption spectra [4]. The extraction coefficient called "recovery rate" (η), which is defined as ratio between the suspension absorbance before and after the EPD process and represents the efficiency of the material usage was calculated.

The suspension depletion during the EPD process was investigated by the same authors. The temporal dependence of the peak absorbance during electrophoretic deposition in a suspension containing 90% of acetonitrile at various applied voltages was studied. It was found that the values in the early stages of deposition can be fitted by single exponential functions. The dependence of η on the acetonitrile content during EPD from toluene/acetonitrile suspensions was also studied [4]. It has been found that η decreases with decreasing acetonitrile content.

* To whom all correspondence should be sent:
E-mail: zhivkov@fch.vutbr.cz

According to the author's knowledge a little could be found in the literature, about the kinetics of the suspension particle formation and growth. This article presents a comparative study of the kinetics investigated by two methods UV-VIS and Dynamic light scattering (DLS).

EXPERIMENTAL

Stock solution (concentration of 0.0495 g/l) was prepared by dissolving 1 mg poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) in 20 ml toluene. 1.5 ml toluene/acetonitrile electrophoretic suspension with MDMO-PPV concentration of 0.0033 g/l containing 45% toluene by volume was prepared diluting of 0.1 ml stock solution (concentration of 0.0495 g/l) with 0.725 ml of pure toluene, followed by addition of 0.675 ml acetonitrile. The mixture was shaken 10 s for a homogenization.

For a comparison 1.5 ml solution with the same MDMO-PPV concentration of 0.0033 g/l was prepared adding 1.4 ml of pure toluene to 0.1 ml stock solution with a concentration of 0.0495 g/l.

Optical absorption spectra of the solution and suspension prepared were measured by a Varian Cary 50 UV-VIS dual beam spectrophotometer. The measurements were carried out in a quartz cuvette with an optical path of 10 mm. The baseline for the UV-VIS measurements was taken from a cuvette, filled with pure toluene or toluene/acetonitrile mixture containing 45% toluene by volume. The spectra in the range of 600-310 nm were measured.

A correct calculation of the derivative from experimental data requires smoothing the noise. The cubic spline procedure [5] has the advantages of derivative calculation and smoothing of almost an arbitrary dataset controlling the spline depth. As a criterion for a correct choice of the spline depth in a way to distinguish the meaningful data from the noise a subsequent recovering of the spectrum was applied.

In Fig. 1 a typical spectrum measured (Fig. 1a), the first derivative (Fig. 1b), determined by a cubic spline procedure and the recovered from the first derivative spectrum (Fig. 2c) are presented. The good coincidence between the experimental data (Fig. 1a) and the recovered by digital integration curve (Fig. 1c) confirms the correct choice of the spline depth parameters, i. e. the first derivative curve calculated (Fig. 1b) represents correctly the experimental data.
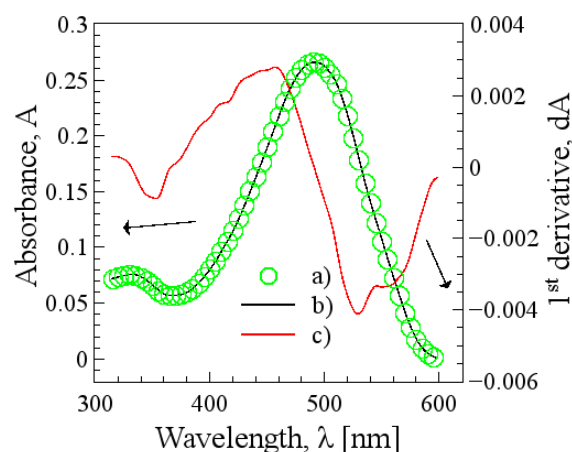
Fig. 1. Derivative calculation: a) – typical characteristic peak of MDMO-PPV (splined data), b) – the first derivative of the data, c) – the spectrum recovered from the first derivative curve.

DLS measurements of suspension with the same parameters as used in UV-VIS experiments were carried out in the same quartz cuvette at 25 ºC. The averaged data were reprocessed taking into account the correct parameters of a toluene/acetonitrile mixture with a content of 45% toluene by volume. The parameters used, i. e. the viscosity of 0.3492 cP, dielectric constant of 30.32 [6] and refraction index of 1.3996 [7] were determined by an approximation from literature data.

RESULTS AND DISCUSSION

UV-VIS absorption spectra of solution and suspension were measured as a function of the time. The first derivatives, calculated according to the aforementioned procedure are presented in Fig. 2. For a sake of clarification the curves obtained from measurement at 100, 215, 440, 2150 and 4635 s are omitted. Comparing the spectrum taken from solution a slight broadening of the low energy ("red") shoulder of the characteristic peak in the suspension spectra was observed.

The first derivatives in the vicinity of the "red" side inflection point are plotted with more details on the inset in Fig 2. It is seen that the shape of the peak around the inflection point is changed progressively with increasing the time.

The absorbance at the inflection point (the values of the minimum from the first derivative curves, see the inset in Fig. 2) is plotted as a function of the time in Fig. 3 (left Y axes). It is seen that a monotonic and almost linear increase of the absorbance with the time is taking place.
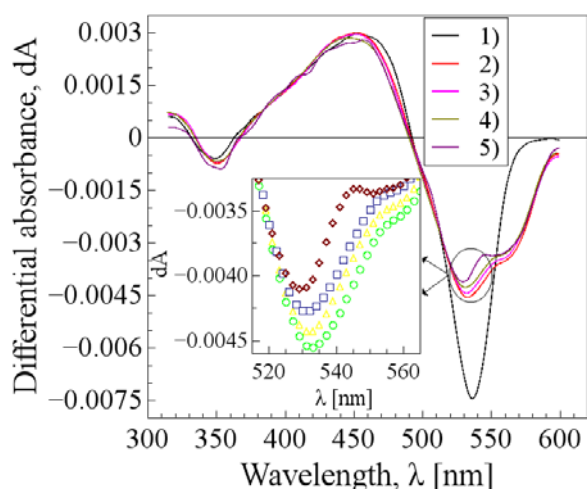
Fig. 2. The first derivatives of the absorbance spectra, measured at different times after the suspension preparation. Inset: part of the absorption spectra of suspensions indicating the changes in the vicinity of the inflection point: (ellipse) – curve 2) measured at 33 s, (triangle) – curve 3), measured at 1000 s, (rectangle) – curve 4) measured at 3500 s, (diamond) – curve 5 measured at 10000 s.
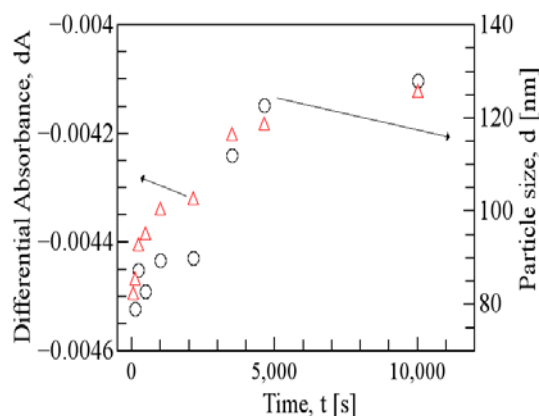
Fig. 3. Kinetics of the absorbance, measured at the inflection point on the "red" side of the maximum of the MDMO-PPV characteristic peak (left Y axes); kinetics of the particle growth in MDMO-PPV suspension, measured by DLS (right Y axes).

The suspension particle size was determined by DLS experiment. In Fig. 3 (right Y axes) the kinetics of the suspension particle growth is presented. It is clearly seen that a progressive suspension particle growth with increasing the time is taking place.

Comparing the kinetics of the UV-VIS absorbance and the kinetics of the suspension particle growth, obtained by DLS experiment a similar dependence could be observed.

These similarities could represent the same or similar processes. It is known that the broadening and the shift of the characteristic peak in UV-VIS spectra of polymers are usually connected with the

presence of a solid phase [8]. Therefore, the changes in the vicinity of the inflection point on the "red" side of the characteristic peak maximum, observed in Fig. 2 should be related to the formation of suspension. On the other hand the DLS experiment directly determines the suspension particle size, which increases with increasing the time. Therefore it could be concluded that the similarities in the curves (Fig. 3), measured by both methods should be related to a formation of the particles in the suspension and the increase of their size as a function of the time. The nonlinear dependence of both curves, presented in Fig. 3 shows that more complicated processes of the particle formation and growth are taking place. This slight nonlinearity could be connected with a possible precipitation of the solid phase which increases progressively with increasing the particle size. The origin of this nonlinearity could be a subject of further investigation.

It could be concluded that the progressive suspension particle growth observed by DLS correlates with the changes in the first derivatives of the UV-VIS spectra. On the basis of this correlation it could be suggested that the UV-VIS measurement, combined with spline and the first derivative calculation could be successfully used for a characterization of the electrophoretic suspensions, namely, for a simple and satisfactory determination of the suspension particle size.

CONCLUSION

The shape of the low energy part of the characteristic absorption peak observed in the first derivative of the spectrum changes in the vicinity of the inflection point regularly with the time. It could be connected with the change of the amount of the solid phase in the toluene/acetonitrile suspension.

Dynamic light scattering measurements confirm the increase of the amount of the solid phase in toluene/acetonitrile suspension with the time, observed as an increase of the particle size. The comparison of both methods shows that UV-VIS spectroscopy could be used as a fast and simple method for a characterization of electrophoretic suspensions indicating indirectly the particle size.

REFERENCES

1. K. Tada, M. Onoda, *Thin Solid Films*, **518**, 711 (2009).
2. K. Tada, M. Onoda, *Jpn. J. Appl. Phys.,* **42**, L1279 (2003).
3. K. Tada, M. Onoda, *Synth. Met.,* **152**, 341 (2005).
4. K. Tada, M. Onoda, *J. Phys. D: Appl. Phys.,* **42**, 172001, (2009).
5. В. А. Василенко, Сплаин-функции: Теория, альгоритми, программи, Наука, Новосибирск, 1983.
6. G. Ritroulls, N. Papadopoulos, and D. Jannakoudakls, *J. Chem. Eng. Data*, **37**, 146 (1986).
7. A. K. Shams, *J. Al-Nahrain Univ.*, **14**, 75 (2011).
8. O. Mirzov and I. G. Scheblykin, *Phys. Chem. Chem. Phys.,* **8**, 5569 (2006).

ОПТИЧНИ ИЗМЕРВАНИЯ НА КИНЕТИКА НА ЕЛЕКТРОФОРЕЗНИ СУСПЕНЗИИ

В. Сидеров[1], Р. Йорданов[2], И. Йорданова[2], С. Бояджиев[3], М. Вала[1], В. Миленков[1], П. Хайнрихова[1], М. Вайтер[1], И. Живков[1, 4]

[1]Технологичен университет – Бърно, Химически факултет, Център по материалознание, ул. Пуркиньова 118, 612 00 Бърно, Чешка република
[2]Технически университет – София, Факултет по електронна техника и технологии, Катедра Микроелектроника, бул. Климент Охридски 8, 1000 София, България
[3]Университет по технологии и икономика – Будапеща, Катедра по неорганична и аналитична химия, Изследователска група по техническа аналитична химия на Унгарската академия на науките, Мюуедйетем пристан 4, 1111 Будапеща, Унгария
[4]Институт по оптически материали и технологии "акад. Й. Малиновски", Българска академия на науките, ул. акад. Г. Бончев, бл. 109, 1113 София, България

(Резюме)

Електрофорезното отлагане (EPD) е метод за получаване на покрития, например в автомобилната индустрия. Понастоящем EPD се използва успешно за отлагане на тънки слоеве с приложения в оптиката и електрониката. В тази статия се изследва процеса на формиране и нарастване на частиците чрез спектроскопия в ултравиолетовата и видимата и област (UV-VIS) и чрез динамично разсейване на светлина (DLS). Суспензиите са формирани чрез утаяване на разтвор на poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] в тулол чрез добавяне на утаител – ацетонитрил. Въз основа на получените резултати може да се направи заключение, че прогресивното нарастване на частиците, наблюдавано с DLS може да бъде установено и чрез първата производна на UV-VIS спектри, след изглаждането чрез сплайн процедура, тоест, UV-VIS спектроскопията може успешно да се използва за оценка на свойствата на електрофорезни суспензии.

Ключови думи: Характеризиране на електрофорезни суспензии, спектроскопия в ултравиолетовата и видимата област, динамично разсейване на светлина, кинетика на растежа на частиците в суспензията.