Characterization of electrophoretic suspension for thin polymer film deposition

D Mladenova¹,²,₅, M Weiter¹, P Stepanek³, I Ouzzane¹, M Vala¹, V Sinigersky⁴ and I Zhivkov¹,²

¹ Centre for Materials Research, Faculty of Chemistry, Brno University of Technology, 118 Purkynova, 612 00 Brno, The Czech Republic
² Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 101, 1113 Sofia, Bulgaria
³ Department of Supramolecular Polymer Systems, Institute of Macromolecular Chemistry, Academy of Sciences of The Czech Republic, 2 Heyrovského nam., 162 06 Praha 6, The Czech Republic
⁴ Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 103A, 1113 Sofia, Bulgaria

E-mail: dnl@clf.bas.bg

Abstract. The optical absorption and fluorescence spectra of poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] toluene solutions and 50:50% toluene/acetonitrile suspensions show clearly distinguishable differences (e.g., peak broadening and shifting), which could be used for characterization of suspensions with different acetonitrile content. The dynamic light scattering (DLS) measurement of the suspensions showed a particle size of 90 nm. Thin films with thicknesses of about 400 nm were prepared by electrophoretic deposition (EPD) and spin coating. As the films are very soft, a contactless optical profilometry technique based on chromatic aberration was used to measure their thickness. AFM imaging of spin coated and EPD films revealed film roughness of 20÷40 nm and 40÷80 nm, respectively. The EPD film roughness seems to be less than the suspension particle size obtained by DLS, probably due to the partial film dissolving by the toluene present in the suspension.

1. Introduction

Among the variety of the methods for “wet” polymer thin film deposition [1] (e. g. spin and dip coating, spray and Langmuir-Blodgett deposition, and ink-jet printing), the electrophoretic deposition (EPD) [2] has the advantages of using a diluted suspension for deposition of relatively thick films, ability for covering a large area and the unique property of separating the solidification stage (precipitation of a solid phase in the suspension) from the film formation stage, which takes place on the electrode.

One of the main problems impeding the wide usage of EPD for thin polymer film preparation is the instability – the suspension particle size depends strongly on the precipitation conditions and tends to

⁵ To whom any correspondence should be addressed.
grow with the time. This effect creates difficulties in controlling the EPD thin film structure and morphology.

This study aims to establish methods for characterization of critical stages of the EPD process of deposition of thin poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) films.

2. Experimental details
The EPD suspension with MDMO-PPV (Sigma-Aldrich, catalogue number 546461) concentration of 0.0033 g l\(^{-1}\) and toluene/acetonitrile ratio of 50:50% (toluene 99.8%, acetonitrile 99.8%) was prepared and used immediately for measurement or deposition to prevent further particle coagulation.

Dynamic light scattering (DLS) measurements of the suspension prepared were performed on a Malvern Zetasizer Nano ZS instrument equipped with a helium-neon laser; the scattering angle was 173°. The data were processed taking into account the viscosity of the toluene/acetonitrile mixture with 50% acetonitrile content [3].

The EPD thin film was deposited on the positive electrode at a current of about 50÷70 µA.

A solution with concentration of 8.95 g l\(^{-1}\) was prepared and spin coating at approx. 2500 rpm for 60 s was carried out on a KW-4A Chemat Technology Inc. spin coater.

The film thickness of the deposited MDMO-PPV films was determined by a MicroProf® FRT optical profilometer based on chromatic aberration. The method has the advantage of performing fast high-resolution contactless and non-destructive measurements, which is of paramount importance in our case of soft polymer films. The films were scratched by a sharpened tungsten wire then a thin (about 100 nm) Al film was deposited in vacuum to equalize the optical reflection from both scratched and unscratched areas.

Surface morphology images of MDMO-PPV films were taken by NTEGRA Prima AFM. The measurements were carried out in semicontacting mode (frequency of 170 kHz, amplitude 80÷100 nm and scanning rate of 0.5 Hz).

3. Results and discussion
3.1. Suspension characterization
3.1.1. Absorption spectra. Optical absorption spectra of a solution and a 50:50 % toluene/acetonitrile suspension with the same MDMO-PPV concentration of 0.0033 g l\(^{-1}\) are presented in figure 1. The solution spectrum (curve 1) consists of the characteristic MDMO-PPV absorption peak [4].

In the suspension (curve 2) spectrum, a “red” shoulder appears which leads to a broadening of the peak. This effect could be related to the appearance of a precipitated solid phase during the suspension formation caused by the precipitating polar acetonitrile.

![Figure 1. Absorption spectra of a MDMO-PPV solution (curve 1) and a suspension with 50% acetonitrile content (curve 2).](image1)

![Figure 2. Fluorescence spectra of a MDMO-PPV solution (curve 1) and a suspension with 50% acetonitrile content (curve 2).](image2)
3.1.2. **Fluorescence spectra.** More detailed information about the material under study can be obtained from the fluorescence spectra, as they present information from two processes – absorption and subsequent emission. In figure 2, fluorescence spectra of a MDMO-PPV solution (curve 1) and a suspension with 50% acetonitrile (curve 2) are plotted. The maximum of the spectrum in the suspension is “red” shifted by about 30 nm. The spectrum shift reflects more precisely the formation of the solid phase.

It could be concluded that effect of the peak broadening in the absorption spectra could be used for a qualitative estimation of the suspension properties, while the peak shifts in the fluorescence spectra yield more detailed information about the formation of a solid phase in the suspension.

3.1.3. **Dynamic light scattering.** The size of the particles forming the solid-state phase in the toluene/acetonitrile suspension with 50% acetonitrile content was estimated by DLS. The typical correlation function obtained (figure 3) allows a straightforward determination of the particle size. The inset in the figure presents the particle size distribution by the intensity obtained using inverse Laplace transformation. The data obtained indicate an average particle diameter of 90 nm.

3.2. **Thin film characterization**

3.2.1. **Optical profilometer film thickness measurement.** Figure 4, a) and b) present scanned optical aberration images of a scratched MDMO-PPV. The scratched area is clearly distinguished, which allows a satisfactory film thickness determination. A film thickness of about 400 nm was determined by processing the data from a single profile line (figure 4, c). Optical-aberration 3D and 2D images can be used as a preliminary film-surface morphology estimation.

A film thickness of about 400 nm was measured by the same procedure for the spin-coated films.

3.2.2. **AFM imaging.** 2D and 3D AFM images of EPD deposited films are shown in figure 5. The surface roughness observed is less than but comparable to the particle size as obtained by DLS. Despite the general assumption that the size of the particle in the suspension should be preserved after EPD of a film [5], partial dissolving of the particles deposited on the substrate by the solvent (50% toluene in the suspension) is possible, which decreases the film roughness. Thus, varying the toluene/acetonitrile ratio gives an opportunity to control the film roughness.

For comparison, the AFM image of a spin-coated film with similar thickness is presented in figure 6. The picture shows a predominant film surface roughness of 20÷40 nm, which is smoother than the surface of the EPD film. The peaks observed with height approx. 50÷70 nm could be connected with the presence of undissolved or aggregated MDMO-PPV particles due to the relatively high solution concentration.
Conclusions
A combination of experimental methods was applied to the characterization of the different stages of the polymer electrophoretic deposition process. The methods could be used to control the suspension stability and the film structure and morphology, which are critical parameters during the EPD of thin polymer films for solar energy conversion purposes.

Acknowledgments
This work was supported by the South Moravian Region and the 7th Framework Program for Research and Development (Grant SIGA 885), and by the Bulgarian National Science Fund at the Ministry of Education, Youth and Science (Grant DO 02-254).

References
[1] Tada K and Onoda M 2009 Molecular Crystals and Liquid Crystals 505 124-9
[2] Boccaccini A R and Zhitomirsky I 2002 Current Opinion in Solid State and Materials Science 6 251-60
[3] Rltroulls G, Papadopoulos N and Jannakoudakis D 1986 J. Chem. Eng. Data 37 146-8
[4] Quoc T V 2006 Electrophoretic deposition of semiconducting polymer metal/oxide nanocomposites and characterization of the resulting films (Dresden Technischen Universität Dresden Germany) p 109
[5] Landfester K, Montenegro R, Scherf U, Gqnter R, Asawapirom C, Patil S, Neher D and Kietzke T 2002 Adv. Mater. 14 651

Figure 5. AFM 2D and 3D images of an EPD film measured on a 5×5 µm scanned area.

Figure 6. AFM 2D and 3D images of a spin coated film measured on 5×5 µm scanned area.