Directed modification of the properties of vacuum deposited polymer layers by energy-stimulated processes

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Abstract. Vacuum deposited thin layers were investigated for obtaining nanocomposite films based on a polyimide matrix and copper phthalocyanine particles as “guests”. The paper presents a study related to energy-stimulated processes using microwave treatment as an alternative to the classical thermal processing. FTIR spectroscopy investigations demonstrated the possibility for a considerable shortening of the entire treatment process. The best results were obtained by combining the thermal and microwave treatments (15 min microwave + 15 min thermal treatment).

1. Introduction
Polyimides (PI) belong to the important class of organic materials known as “high performance” polymers due to their exceptionally high thermo-oxidative stability [1]. They are especially suitable for the role of a nano-composite matrix owing to their chemical inertness and high thermal stability [2]. The application of energy-stimulated processes for thin layer formation is a modern tendency in the nanotechnology field. Our previous papers [3,4] demonstrate the use of electron–assisted deposition (EAD) of PI precursor layers and this new type of process for production of nanocomposite layers on the basis of a PI matrix. The possibility for low–molecular compound cluster formation in EAD was suggested. The embedding of these clusters in the thin PI layer matrix can lead to a higher value of the dielectric constant. At the same time, the electron influence results in annealing of structural defects and formation of layers with less non-perfections. A large number of articles have been published dealing with the influence of energy-assisted treatment, e.g., the impact of glow discharge vapour deposition [5] on the properties of the main polymer product prepared. In the work reported here our attention was only focussed on the vacuum deposition of polyimide precursors and on the subsequent thermal treatment finalizing the imidization [6].

Microwave (MW) irradiation which also belongs to the energy-stimulated processes is of an increasing interest. It offers a clean, cheap and convenient method of heating which often results in higher yields and shorter reaction times. MW irradiation has found new and increasing applications in organic synthesis for optimizing and accelerating chemical reactions [7] and for selective heating of

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adsorbed phases [8]. The MW technique can be successfully applied in all cases when materials containing polarizable molecules should be thermally treated. It is clear that MWs are not a panacea but used correctly they can be of colossal benefit to the chemist saving both time and money [9]. The MW technology has potential advantages for thin layer materials, in which an application of thermal treatment is incumbent and especially for polymers in which thermal conductivity is particularly poor and large thermal gradients are generated during fast heating rates thus causing excessive internal tensions.

The present study deals with the possibility for applying energy-stimulated processes based on MW treatment of the vacuum deposited (VD) thin layers for obtaining nanocomposite films on the basis of a PI matrix and embedded particles of copper phthalocyanine (CuPc) as “guests”.

2. Experimental
The films investigated were 500-nm thick nanocomposite layers (PI / 9% CuPc). They were formed by vacuum co-deposition of the PI precursors - oxidianiline (ODA) and pyromellitic dianhydride (PMDA) - from two independent thermally heated Knudsen-type vessel sources. CuPc was evaporated at the same time from a SIMAX glass crucible. The evaporation temperatures were 120 – 145°C for PMDA, 100 – 110°C for ODA and 400 – 450°C for CuPc. The evaporation flows were measured separately with quartz microbalance sensors and mixed in the substrate area in a desired ratio. The deposition rates of 0.2 to 10 Å/s were kept in a constant ratio by means of computer driven feedback [10]. The substrate was moved linearly with a speed of about 1 mm/s. After deposition, the samples were treated as follows: 15 min MW + 15min or 60 min thermally at 200°C [11]. A specially developed system was used for the MW treatment (2,45 GHz, 700 W). The samples were MW treated by fixing them at an equal distance perpendicular to the direction of the MW propagation in a holder transparent for the MW radiation.

FTIR (Fourier Transform Infrared Spectroscopy) spectra (deposited layers on KBr substrates, pellets of a diameter of 13 mm) were recorded on a Perkin Elmer 1600 spectrometer in the range 3600-450 cm⁻¹. For each sample 1028 interferograms were collected, signal averaged and Fourier transformed to generate spectra with a nominal resolution of 4 cm⁻¹. The degree of imidization was determined by comparing the 1380 cm⁻¹ peak intensity normalized to the 1500 cm⁻¹ peak intensity [12].

3. Results and discussion
The FTIR spectroscopy results on the pure thin CuPc layers (figure 1) indicate that after a 15 min MW treatment (Pr1) CuPc is in two polymorph forms, namely, β (799 cm⁻¹) and α (722 cm⁻¹). The β form predominates. The frequency and intensity distribution patterns of the absorption between 700-800 cm⁻¹ and 1090-1180 cm⁻¹ are unique for each polymorph. Since these frequencies correspond to the out-of-plane C-H bending modes of the peripheral benzene rings of the CuPc molecule, the orientation of adjacent molecules, which in turn determines the polymorphic phase, has a definite effect on these absorption frequencies [13]. Upon applying additional thermal treatment (Pr2 and Pr3) the α form is prevalent. The duration of the thermal treatment does not change the type of the IR spectra (Pr2 and Pr3). A 15 min thermal treatment is sufficient. The C=N-C stretch at 1260 cm⁻¹ is characteristic for all five modifications of CuPc [14]. Surprisingly this band decreases drastically in the spectra Pr2 and Pr3. The modifications observed of the VD layer properties are probably due to the thermal processes intensified by the MW treatment applied preliminarily.

The FTIR spectra of VD composite (PI / 9% CuPc) layers are presented in figure 2. In spectra Pr2 and Pr3 the bands at 1721 cm⁻¹ correspond to imide I asym. C=O stretch [15]. The bands at 1382 cm⁻¹ characterize the imidization process. The bands at 1116 cm⁻¹ in the same spectra correspond to imide
(OC)$_2$NC deformational vibrations and present an additional evidence for imidization and allows one to assess indirectly the layer quality. On the other hand, the duration of the thermal treatment (Pr2 and Pr3) does not have a significant impact. The band at 1382 cm$^{-1}$ in spectrum Pr3 is narrow and more intensive while in the spectrum Pr2 it is of lower intensity and is shifted negligibly by 4 cm$^{-1}$.

**Figure 1.** FTIR spectra of VD 100 nm thick CuPc layers: Pr1- 15 min MW treated; Pr2- 15 min MW treated + 15 min treated at 200 °C; Pr3- 15 min MW treated+60 min treated at 200 °C.

**Figure 2.** FTIR spectra of VD 500 nm thick composite (PI/ 9% CuPc) layers: Pr1- 15 min MW treated; Pr2- 15 min MW treated + 15 min thermally treated at 200 °C; Pr3- 15 min MW treated + 60 min thermally treated at 200 °C.

MW treatment only does not improve the imidization degree [11] and does not affect the quality of the composite layer (figure 2 - Pr1). The bands do not correspond to the bands of spectra Pr2 and Pr3. It is logical to conclude that the combination of MW and thermal treatment only may considerably decrease the time of the layer post-deposition treatment.
4. Conclusion
These initial investigations show that the MW processing of polymers combines the rare opportunity to perform fundamental research aimed at understanding the processes with a potential for a significant commercial success and impact on the area of materials processing. The results from the investigations performed confirm the possibility of a directed modification of the VD layer properties and shortening the time of post-deposition treatment of nanocomposite layers by energy-stimulated processes based on MW treatment. MW irradiation helps the formation of high-quality CuPc layer. The combination of MW and thermal treatment decreases the entire post-deposition process by half an hour (from 60 min [16] to 30 min). The optimization of the MW processes used in thin layer nanocomposites will be the subject of our future investigations.

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