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Spectroscopic investigation of different concentrations of the vapour deposited copper phthalocyanine as a "guest" in polyimide matrix

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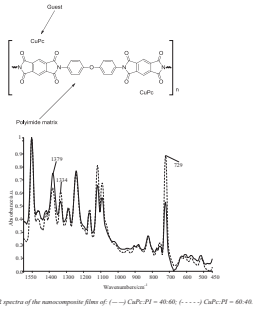
HIGHLIGHTS

- Different concentrations of copper phthalocyanine in polyimide matrix have been investigated in nanocomposite films.
- FTIR spectroscopy has been applied for quantitative and qualitative analysis of the CuPc in PI/CuPc composites.
- The relationship between structure and spectral properties has been studied.

GRAPHICAL ABSTRACT

FTIR spectra of the nanocomposite films of: (——) CuPc:PI = 40:60; (- - - - -) CuPc:PI = 60:40.



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ABSTRACT

Nanocomposite layers 250 nm copper phthalocyanine/polyimide prepared by simultaneous vapour deposition of three different sources were studied. Different concentrations of copper phthalocyanine as a "guest" in polyimide matrix as a function of conditions of the preparation have been determined by FTIR (Fourier Transform Infrared) and UV–VIS (Ultraviolet–Visible) spectroscopies. The aim was to estimate the possibility of the spectroscopic methods for quantitative determination of the "guest" and compare with the quality of the polyimide thin films in relation to the "guest" concentration. The band at 1334 cm^{-1} has been used for quantitative estimation of "guest" in polyimide matrix. The concentrations of the copper phthalocyanine less than 20% require curve fitting techniques with Fourier self deconvolution. The relationship between "guest" concentrations and degree of imidization, as well as the electronic UV–VIS spectra are discussed in relation to the composition, imidization degree and the two crystallographic modification of the embedded chromophore.

Introduction

Nanocomposite materials generally, represent combinations of substances – polymers, chromophores, metals, etc. in which one component is the matrix and the other one is the "guest", embedded in the matrix as nanosized particles. The preparation of new nanocomposite materials is important because the combination of different solid phases makes synergistic modification of the component properties. The preparation of organic nanocomposite films could be by simultaneous vapour deposition of the different precursors, by multi-source physical vapour deposition and next

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solid state reactions [1,2]. The obtained films using the vacuum technologies ensure one basic advantage – the absence of solutions and elimination of the necessity of complicated technical methods for their removal [3]. Over the past decade, the interest in thin organic films has grown dramatically due to their successful application in optical and electronic devices, such as light emitting diodes, field effect transistors, organic solar cells, etc. [4]. The development of chemistry of polymer thin films is currently subject of intense fundamental and technological interest. One of the achievements is reactions of the solid state polymerisation, when the starting precursors are deposited on the substrate [5]. A typical example for solid state reaction is the synthesis of the polyimide by vapour deposition of the precursors ODA (4,4′-oxidianiline) and PMDA (pyromellitic dianhydride) and next thermal treated of nanosized film to imidization. There are enough convincing results confirming the assumption that the polycondensation reaction between the precursors ODA and PMDA could be accelerated also by energy treatment like microwave [6].

Polyimides (PI) have the capacity to be nanocomposite matrix due to their high chemical and thermal stability and suitable optical and dielectric properties [3,7,8]. Aromatic polyimides are well-known polymers due to their properties such as a low dielectric constant, high thermal stability, high chemical resistance, high optical transmittance as well as very good mechanical properties. There are evidences that polyimides are biocompatible materials and used for preparation of medical devices and especially for encapsulation and insulation of active neural implants. Their application in clinical practice has given rise to the fields known as "neuromodulation" and "neuroprosthetics" or neural prostheses [9–11].

In the last decades there are many convincing results, which confirmed the applicability of the polyimides in the field of the material science [1–3]. They are combination of matrix, such as PI and embedded nanosized particles of different metals, salts or dyes, as the "guest" [1,2]. The combination of PI matrix with embedded "guest" such phthalocyanines offer wide way for desired changes of the optical, electrical properties of the nanocomposite films [5,12,13]. Phthalocyanines are aromatic organic compounds having semiconducting properties. The metal phthalocyanines especially copper phthalocyanines (CuPc) are important optical and semiconducting materials with excellent thermal and chemical stability. Their unique semiconducting properties, the possibility of modifying their conduction optically or chemically, and strong absorption in visible to near infrared region have made them not only wonderful gas sensors, but also promising organic electrophotographic materials, nonlinear optical materials and optical recording materials [14–17]. Moreover, the CuPc brings new possibilities for biosensors construction and for developing novel electrochemical bioassays [14,18].

The crystalline structure of phthalocyanine compounds is of high stability that can be found in several crystalline polymorphic forms [15–17,19]. The FTIR spectroscopy is a powerful tool to study orientation, sub-cell packing and the structure of hydrocarbon chains in the evaporated films and quantitative determination of chromophores in thin films [7]. The intensities of bands provided information about the orientation changes due to the distortions of molecules. The FTIR spectroscopy has also been used to study the crystalline nature for both powder (as bulk materials) and CuPc/PI thin nanocomposite films. The change of bands in the range of molecular vibration of the CuPc is due to the interaction between molecules with each other as well as the interaction of the chromophore with PI matrix [20].

In the present work, structural properties of vacuum deposited nanocomposite films prepared by copper phthalocyanine as a "guest" and polyimide as a matrix (CuPc/PI) were studied. The aim was to demonstrate the possibilities of the Fourier Transform Infrared (FTIR) and Ultraviolet Visible (UV–VIS) spectroscopies for determining the concentrations of the CuPc in composite PI/CuPc films as well as the influence of the chromophore on their spectral properties.

Experimental

FTIR spectroscopy

FTIR spectra of the vapour deposited nanocomposite PI/CuPc films on a KBr substrate have been recorded on a Bruker Tensor 27 FTIR spectrophotometer in the range 4400–600 cm^{-1} with resolution 2 cm^{-1}. All films used in this study were 250 nm thick and so they were sufficiently thin to absorb in the range where the Lambert–Beer law is obeyed. The spectra were normalised to the 1500 cm^{-1} peak intensity [6]. The band was chosen because the quantity of the –C–C– stretching vibrations groups had not changed during the imidization. Each complex bands were analysed by Fourier Self Deconvolution. The spectra have been subjected to a line shape analysis by the GRAMS and SpekWin32 software.

UV–VIS spectroscopy

UV–VIS spectra were measurement on a Varian-Carry 300 spectrophotometer at room temperature in the range 200–1000 nm. For these studies the nanocomposite PI/CuPc vapour deposited samples were prepared on a Si-substrate. All spectra were performed in transmittance.

Preparation of thin nanocomposite films

Thin films of thickness 250 nm were deposited simultaneously on to KBr optically flat substrate and on Si-substrate. The thin PI layer matrix was performed by vacuum co-deposition of precursors 4,4′-oxidianiline (ODA) and pyromellitic dianhydride (PMDA) from two independent thermally heated Knudsen-type vessel sources on linearly moving substrates. The ODA/PMDA molar ratio was 1:1. CuPc was evaporated at the same time from SIMAX glass crucible. In this way the CuPc "guest" was uniformly distributed into the matrix. The base pressure was kept at 5×10^{-4} Pa. The evaporation temperatures were 120–145 °C for PMDA, 100–110 °C for ODA, 400–450 °C for CuPc and deposition rates were in the range of 0.2–10 A/s. The substrates were linearly moved with a speed of about 1 mm/s in a way to get homogeneous film along the direction of the movement [23]. The investigated "guest" concentration in the composite layers varied from 20% to 80%. The arrangement of the evaporation system is presented in Fig. 1.

The obtained films were placed successively in a closed chamber for solid state imidization at temperature 200 °C for 1 h. The camera was equipped with an infrared heater and the temperature increased approximately 10 °C per 1 min. The choice of the temperature is based on the minimisation of polymorphic transformation of CuPc over 250 °C. The concentration of CuPc was calculated as weight percentage to PI matrix. Scheme 1 shows the reaction between PMDA and ODA in presence of CuPc as a "guest".

Measurement of thickness

The thickness was measured by profilometer "Talystep" Taylor Hobson. The evaporation rates and the relative final thicknesses of the films were followed by quartz crystal balance. It measures the thickness by traversing the stylus either across a test groove formed in the deposited film. Vertical movement of the stylus is amplified electronically and recorded as a graphical representation