UNIVERSITI PUTRA MALAYSIA

THERMAL DIFFUSIVITY MEASUREMENT AND PHOTOBLEACHING STUDY USING PHOTOACOUSTIC TECHNIQUE AND UV -VISIBLE FIBRE OPTICS SPECTROMETRY

CHAN KOK SHENG

FSAS 2002 35

THERMAL DIFFUSIVITY MEASUREMENT AND PHOTOBLEACHING STUDY USING PHOTOACOUSTIC TECHNIQUE AND UV-VISIBLE FIBRE OPTICS SPECTROMETRY

By

CHAN KOK SHENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in fulfillment of Requirement for the Degree of Master of Science

September 2002

Abstract of the thesis presented to the senate of Universiti Putra Malaysia in fulfillment of requirements for the degree of Master of Science

THERMAL DIFFUSIVITY MEASUREMENT AND PHOTOBLEACHING STUDY USING PHOTOACOUSTIC TECHNIQUE AND UV-VISIBLE FIBRE OPTICS SPECTROMETRY

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Chairman: Professor W. Mahmood Bin Mat Yunus, Ph.D.

Faculty: Science and Environmental Studies

In recent years, the photoacoustic effects in solid materials, induced by the absorption of intensity-modulated laser radiation, were used as a versatile tool for optical and thermal characterization of a variety of samples. In our work, by using the photoacoustic detection technique, the measurement was first carried out to obtain the thermal diffusivity values of commercial papers (i.e. white paper, drawing paper, filtering paper, wrapping paper, fax paper and press paper), sago starch, chitosan and the blends of sago starch with chitosan. All the measurements for these samples were carried out at room temperature. It was based upon the measurement of the photoacoustic signal as a function of the modulation frequency in the region where the thermal diffusion length equals to the sample thickness. The results showed that the measured thermal diffusivity values for commercial papers and the blends of sago starch with chitosan were in the range of 0.50×10^{-3}-12.0×10^{-3} cm^2s^{-1} and 1.44×10^{-3}-2.01×10^{-3} cm^2s^{-1}, respectively. We also measured the photostability of Rhodamine 6G(R6G) dye doped in poly(methylmethacrylate)

PMMA polymer matrices. The present investigation indicates that the R6G-doped PMMA samples are still photostable under irradiation at laser beam less than 300mW.

Furthermore, the photoacoustic detection technique were also used to investigate the photobleaching process of the methylene blue (MB) organic dye embedded in the polymer matrices of Poly(vinyl alcohol)(PVA), poly(methylmethacrylate) PMMA, gelatin, sago starch and chitosan. Photoacoustic investigation for photobleaching process was also investigated in sago starch blend with chitosan. We observed a significant decrease in the PA signal amplitude with respect to time for these samples during the beginning of irradiation, which is mainly due to the photodegradation of the MB dye molecules from their original state. The photobleaching rate for each sample is directly proportional to the incident laser power and it decreases with the increasing the concentration of the dye molecules. For these samples, the thermal diffusivity value has been determined from the phase-frequency dependant relation after two hours of laser irradiation. Subsequently, by using the single beam uv-visible fibre optics spectrophotometer, we also investigated the photobleaching effect by measuring the variation of the absorption peak for these samples upon continuous uv-visible radiation. From the observation, the MB dye molecules undergo the photodegradation process due to the decrease of absorption peaks with exposure time. The observed new band in the Raman spectra after laser irradiation for each bleached sample confirmed the formation of the leuco MB (colorless) in the polymer matrix. The photochemical mechanisms were discussed for MB degradation in polymer, which involve the photoexcitation process, redox reaction and quenching process.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENGUKURAN RESAPAN TERMA DAN FOTOPELUNTURAN DENGAN MENGGUNAKAN TEKNIK FOTOAKUSTIK DAN SPEKTROMETRI OPTIK GENTIAN UV-CAHAYA NAMPAK

Oleh

CHAN KOK SHENG

September 2002

Pengerusi: Profesor W. Mahmood Bin Mat Yunus, Ph.D.

Fakulti: Sains dan Pengajian Alam sekitar

Sejak kebelakangan ini, kesan fotoakustik di dalam bahan pepejal yang disebabkan oleh penyerapan sinaran laser termodulasi telah digunakan sebagai satu cara yang penting dalam pencirian optik dan terma untuk pelbagai sampel. Dalam penyelidikan kami, dengan menggunakan teknik fotoakustik, kajian mula dilakukan bagi tujuan mendapatkan nilai resapan terma bagi kertas kegunaan kormesial (kertas putih, kertas lukisan, kertas turas, kertas pembalut, kertas faks dan kertas akhbar), kanji sago, kitosan dan adunan antara kanji sago dengan kitosan. Semua pengukuran untuk sampel-sampel ini dilakukan pada suhu bilik. Ia adalah berdasarkan pengukuran isyarat fotoakustik sebagai fungsi frekuensi termodulasi di mana kepanjangan resapan terma adalah sama dengan ketebalan sampel. Keputusan menunjukkan nilai resapan terma untuk kertas kegunaan kormesial dan adunan antara kitosan dengan kanji sago adalah masing-masingnya dalam julat 0.50×10^{-3}-12.0×10^{-3} cm^2s^{-1} dan 1.44×10^{-3}-2.01×10^{-3} cm^2s^{-1}. Selain itu, kami juga mengukur kesan kestabilan foto bagi pewarna organik Rhodamin 6G(R6G) terdop dalam

polimer matrix poli(metil methakrilat) PMMA. Kajian ini menunjukkan bahawa sampel R6G terdop dalam PMMA masih fotostabil di bawah sinaran laser diod kurang daripada 300mW.

Dalam kajian seterusnya, teknik fotoakustik telah digunakan untuk mengkaji proses fotopelunturan pewarna organik metillin biru (MB) terdop dalam matriks polimer iaitu Poli(vinyil alkohol)(PVA), poli(metil metakrilat) PMMA, gelatin, kanji sago dan kitosan. Penyelidikan fotoakustik untuk proses fotopelunturan juga telah dikaji pada adunan kanji sago dengan kitosan. Kami dapati bahawa penurunan ketara dalam amplitud isyarat fotoakustik terhadap masa untuk sampel-sampel ini di awal penyinaran yang mana adalah disebabkan oleh fotodegradasi molekul pewarna MB daripada keadaan asal mereka. Kadar fotopelunturan untuk setiap sampel adalah berkadar langsung kepada kuasa laser terpancar dan berkurangan dengan bertambahnya kepekatan molekul-molekul pewarna organik. Untuk sampel-sampel ini, nilai resapan terma telah didapati daripada fungsi di antara fasa dan frekuensi setelah sinaran laser selama dua jam. Selanjutnya, dengan menggunakan spektrofotometer optik gentian uv-cahaya nampak, kami juga telah mengkaji kesan fotopelunturan ke atas sampel-sampel ini dengan mengukur perubahan puncak penyerapan di bawah penyinaran uv-cahaya nampak secara berterusan. Daripada pemerhatian, molekul pewarna MB telah melalui proses fotopelunturan yang diakibatkan oleh penurunan puncak penyerapan dengan masa penyinaran. Permerhatian jalur baru pada spektra Raman lepas penyinaran laser kepada setiap sampel terluntur menyakinkan pembentukan MB leuko di dalam matriks polimer. Mekanisme fotokimia berkenaan

fotopelunturan MB di dalam polimer, yang mana melibatkan proses pengujaan foton, tindakbalas redoks dan proses penyahujaan turut dibincangkan.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest praise to God who has given me strength, faith, confidence and courage to complete this project within the time frame.

I would like to take this opportunity to convey my sincere thanks and deepest gratitude to my supervisor, Associate Professor Dr. W. Mahmood bin Mat Yunus, who contribute his knowledge, encouragement, help, invaluable advise, ideas, suggestion and constructive criticism with patience throughout this project and to bring this thesis to its final form. I am indeed grateful and consider myself privileged to work under his guidance. I would also like to extend my sincere appreciation and thanks to my co-supervisors Professor Dr. Wan Md. Zin bin Wan Yunus and Associate Professor Dr. Mohd. Maarof bin Moksin for their knowledge, help, encouragement and discussions provided to me during this study.

Thank you is also expressed to my seniors especially Fanny Chin Yee Ju and Teh Ee Ping, all my dear friends and coursemates, who either directly or indirectly, have contributed in a variety ways towards the success of the project.

Finally, I would like to express my sincere gratitude to my father, mother, brothers, sisters, uncle, aunts, cousins, nieces, and nephews for their prayers, love, generous moral and support during my study.

I certify that an Examination Committee met on 12th September 2002 to conduct the final examination of Chan Kok Sheng on his Master of Science thesis entitled "Thermal Diffusivity Mesurement and Photobleaching Study Using Photoacoustic Technique and UV-visible Fibre Optics Spectrometry" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relavant degree. Members of the Examination Committee are as follows:

AZMI ZAKARIA, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

W. MAHMOOD BIN MAT YUNUS, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

WAN MD. ZIN BIN WAN YUNUS, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

MOHD. MAAROF BIN MOKSIN, Ph..D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

SHAMSHER MOHAMAD RAMADILI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 SEP 2002

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement of Master of Science. The members of the Supervisory Committee are as follows:

W. MAHMOOD BIN MAT YUNUS, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

WAN MD. ZIN BIN WAN YUNUS, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

MOHD. MAAROF BIN MOKSIN, Ph..D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professor/ Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

(CHAN KOK SHENG)

Date: 20/9/2002

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LIST OF ABBREVIATION

α	Thermal diffusivity
κ	Thermal conductivity
α_n	Thermal diffusivity of layer n where n can take the subcripts of s(sample), g (gas) and b (backing material)
l_s	Sample thickness
l_g	Gas column thickness
l_b	Thermal conductor thickness
I	Intensity
$I_\bullet$	Incident monochromatic light flux
x	Depth
ω	Modular angular frequency of incident light
β	Optical absorption coefficient of solid sample
λ	Wavelength
θ	Temperature
θ_o	Temperature at solid-gas boundary (x = 0)
θ_{ac}	Periodic temperature change
θ_{av}	Average temperature
η	Efficiency at converting the absorbed light into heat by the nonradiative deexitation process
ρ_n	Density
C_n	Specific heat capacity
$2\pi\mu_g$	Thickness of boundary layer
PV^γ	Adiabatic gas law
δP	Incremental pressure
f	Modulation frequency
W	Radiant power
T	Transmission
A	Absorbance
M	Mass
m_s	Mass of container and liquid sample
m_o	Mass of empty container
V	Volume

CHAPTER 1

INTRODUCTION

1.1 Photothermal and Photoacoustic

Photothermal science encompasses a wide range of techniques and phenomena based upon the conversion of absorbed optical energy into heat. Optical energy is absorbed and eventually converted into thermal energy by an enormous number of materials –solids, liquids, and gases. In fact, when the optical energy is absorbed, the excited states in atoms or molecules loose their excitation energy by a series of non-radiative transitions that results in a general heating in the material.

The underlying principles of the photoacoustic effect have been studied for more than a century. It was named photoacoustic because the photothermal heating effect was detected by an indirect acoustic method. In 1880, Alexander Graham Bell (cited in Favier J.P. 1997) had discovered the early concept of the photoacoustic effect when he tried to explain the operation of his photophone. He had done a lot of experiments on photoacoustic effect with solids, gases and liquids, where modulated light was used to illuminate the sample. Through the experiments, Bell discovered that when a periodically interrupted beam of sunlight shines on a solid in an enclosed cell, an audible sound could be heard by means of hearing tube attached to the cell. The photoacoustic effect discovered by Bell was regarded as a part of the family of photothermal phenomena