

**EFFECTS OF RADIATION ON CONDUCTIVITY AND DIELECTRIC
PROPERTIES OF POLYMETHYLMETHACRYLATE /ACRYLIC ACID
POLYMER BLENDS**

By

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

June 2006

This thesis dedicates to

My mother Sarimah Tambi

&

My late father Mohd Yusof Mat Zin

Al-Fatihah.....

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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The cation exchange membranes seem to be the most widely studied due to their appropriate properties for many applications including as solid polymer electrolytes for electrochemical devices in battery and fuel cell. Polymethylmethacrylate /Acrylic acid (PMMA/AA) blends have been prepared by solvent casting method at different PMMA:AA ratios of 1:1, 1:2, 1:2.5, 1:3.0, 1:3.5 and 1:4.0 by weight. The samples were irradiated separately using 1.25-MeV γ -rays at different doses of 2, 4, 8 and 10 kGy and also with 1.25-MeV e-beam at doses of 50, 100, 150 and 200 kGy. The non-irradiated samples were also treated thermally at different temperatures of 300, 333, 342, 352 and 363 K. The dielectric properties and the electrical conductivity have been studied using an impedance analyzer at frequencies ranging from 20 Hz to 1 MHz. The dc conductivity, σ_{dc} of un-irradiated and thermally untreated samples increases from 7.7×10^{-8} S/m to 3.27×10^{-7} S/m at 100 Hz when the composition ratio increases from 1:2.5 to 1:4 due to an increase of the number of free charge carriers, mainly ions introduced in the blends. The dielectric loss ϵ'' at 100 Hz also increases from 9.32 to

621.03. However, at these concentration ratios, the dielectric constant, ϵ' at 100 Hz decreases from 15.68 to 10.64, attributed to decreasing effect of dielectric dipole as the amount of charge carriers introduced into the system increases. An increase of temperature from 300 K to 363 K increases the dc conductivity of 1:4 composition ratios from 1.1×10^{-5} S/m to 6.91×10^{-4} S/m at 100 Hz due to an increase of the ion mobility and thermal expansion occurred in the blends. By the temperature treatment the value of ϵ'' at 100 Hz also increases from 10.35 to 10.04×10^3 with the temperature increases due to an increase of the mobility of free ions. An increase of ϵ' value at 20 Hz from 10.35 to 15.38 with increasing temperature from 300 K to 363 K is due to increase the degree of dipole orientation as more dipoles in the samples align with the electric field. Upon irradiation with doses from 2 kGy up to 10 kGy, the polymer blends become grafted to Polymethylmethacrylate-g-Polyacrylic acid (PMMA-g-PAA) blends, which increase the dc conductivity of 1:4 composition ratio from 2.13×10^{-7} S/m to 6.07×10^{-7} S/m at 100 Hz as the number of free and trapped ions increases. There is also an increase of ϵ'' value at 100 Hz from 38.43 to 109.27 with the increase of dose from 2 kGy up to 10 kGy, due to the increase of ions within the irradiated materials. At the same time the dielectric constant value of ϵ' at 100 Hz increases from 9.98 to 22.83 as more dielectric dipoles are present due to the increase of grafting. As the dose increases from 50 kGy to 200 kGy after e-beam irradiation, the PMMA/AA polymer blends become PMMA/PAA copolymer composites. The dc conductivity of 1:4 composition ratio increases from 1.9×10^{-9} S/m to 1.29×10^{-8} , when the dose increased from 50 kGy to 200 kGy, since more ions might be generated in the samples. The value of ϵ'' at 100 Hz also increases from 0.34 to 2.32, as more increase ions were introduced

within the materials. The value of ϵ' at 100 Hz increases from 3.03 to 12.92, when the dose increased from 50 kGy to 200 kGy, attributed to the cross-linking between PMMA and PAA, which results in more dipoles formed in the co-polymer matrix.

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

**KESAN RADIASI KE ATAS SIFAT KONDUKTIVITI DAN DIELEKTRIK
BAGI CAMPURAN POLIMER POLIMETILMETA AKRILIK (PMMA)/
AKRILIK ASID(AA)**

Oleh

NORAZIMAH MOHD YUSOF

Jun 2006

Pengerusi : Profesor Madya Elias Saion, PhD

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Kajian berkaitan membran pertukaran kation semakin meluas berdasarkan daripada sifatnya yang menepati dalam kegunaan yang pelbagai termasuk sebagai elektrolit polimer keras untuk kegunaan alat elektrokimia dalam bateri dan sel tenaga. Filem Polymetilmetaakrilik (PMMA)/Akrilik asid (AA) telah disediakan dengan menggunakan teknik acuan pada nisbah PMMA:AA yang berbeza, 1:1, 1:2, 1:2.5, 1:3.0, 1:3.5 and 1:4.0. Sampel diradiasikan secara berasingan menggunakan 1.25 MeV sinar- γ dengan ^{60}Co pada dos berbeza 2, 4, 8 dan 10 kGy, dan juga diradiasikan dengan 1.25 MeV hentaman elektron pada dos yang berlainan, 50, 100, 150 dan 200 kGy. Sampel yang tidak diradiasi dipanaskan pada suhu berbeza 300 K, 333 K, 342 K, 352 K dan 363 K Sifat dielektrik dan konduktiviti dc elektrik diukur dengan menggunakan analisis impedan pada frekuensi berbeza dalam lingkungan 20 Hz ke 1 MHz. Konduktiviti dc sampel yang tidak diradiasi dan dikenakan suhu, meningkat daripada

7.7×10^{-8} S/m kepada 3.27×10^{-7} S/m pada 100 Hz apabila nisbah komposisi meningkat dari 1:2.5 kepada 1:4 disebabkan oleh peningkatan bilangan pembawa cas bebas, terutamanya ion yang terhasil di dalam campuran. Faktor kelesapan dielektrik, ϵ'' pada 100 Hz juga meningkat daripada 9.32 kepada 621.03. Walaubagaimanapun pada nisbah-nisbah konsentrasi ini, pemalar dielektrik, ϵ' pada 100 Hz menurun daripada 15.68 kepada 10.64 hasil daripada kesan penurunan dwikutub dielektrik apabila jumlah cas pembawa terhasil dalam system meningkat. Peningkatan suhu daripada 300 K kepada 363 K meningkatkan konduktiviti dc nisbah komposisi 1:4 daripada 1.1×10^{-5} S/m kepada 6.91×10^{-4} S/m pada 100 Hz, hasil daripada peningkatan kelincahan dan pengembangan terma yang berlaku di dalam campuran. Nilai ϵ'' pada 100 Hz turut meningkat daripada 10.35 kepada 10.04×10^3 dengan suhu disebabkan oleh peningkatan kelincahan ion bebas. Peningkatan nilai ϵ' pada 20 Hz daripada 10.35 kepada 15.38 dengan peningkatan suhu daripada 300 K kepada 363 K kerana peningkatan darjah orientasi dwikutub apabila semakin banyak dwikutub dalam sampel berjajaran dengan medan elektrik. Penradiasian yang dikenakan dengan dos daripada 2 kGy kepada 10 kGy, campuran polimer telah menjalani proses *grafting* menjadi Polimetilmetaakrilik (PMMA)-g-Akriklik asid (AA), (PMMA-g-PAA) yang mana meningkatkan konduktiviti dc dengan nisbah komposisi 1:4 daripada 2.13×10^{-7} S/m kepada 6.07×10^{-7} S/m pada 100 Hz berikutan daripada bilangan ion bebas dan ion terperangkap meningkat. Nilai ϵ'' juga meningkat pada 100 Hz daripada 38.43 kepada 109.27 dengan peningkatan dos daripada 2 kGy kepada 10 kGy, kerana peningkatan ion di dalam sampel yang telah diradiasikan. Pada masa yang sama nilai ϵ' pada 100 Hz meningkat daripada 9.98 kepada 22.83 kerana lebih dwikutub elektrik terhasil

disebabkan proses *grafting*. Apabila dos meningkat daripada 50 kGy kepada 200 kGy hasil dari radiasi hentaman elektron, PMMA/AA campuran polimer menjadi PMMA/PAA komposit kopolimer. Konduktiviti dc nisbah komposisi 1:4 meningkat daripada 1.9×10^{-9} S/m kepada 1.29×10^{-8} , apabila dos meningkat daripada 50 kGy to 200 kGy, hasil daripada lebih elektron dihasilkan dan lebih ion terhasil di dalam sampel. Nilai ϵ'' pada 100 Hz juga meningkat daripada 0.34 kepada 2.32, kerana lebih peningkatan elektron terhasil di dalam bahan. Nilai ϵ' pada 100 Hz meningkat daripada 3.03 kepada 12.92 apabila dos meningkat daripada 50 kGy to 200 kGy, disebabkan berlakunya taut silang di antara PMMA and PAA, yang menyebabkan lebih dwikutub terhasil di dalam campuran kopolimer.

ACKNOWLEDGEMENTS

First of all I am very grateful to Allah the most beneficent and merciful, for giving I full strength to complete this thesis.

I sincerely would like to extend my utmost gratitude to my supervisor, Assoc. Prof. Dr Elias bin Saion, Department of Physics, Faculty Science, University Putra Malaysia, for his immeasurable support, invaluable guidance, generous advice, encouragement and constructive suggestions throughout the course of this project.

My gratitude also to committee member Dr. Jumiah Hassan, Assoc. Prof. Dr. Mohd Zaki Ab. Rahman and Dr. Dahlan Hj. Mohd to provide constructive information, cooperation, valuable assistance and guidance throughout the course of study.

I also wish to acknowledge my gratitude to all lecturers and staffs in department of Physics, Faculty Science and Malaysia Institute of Nuclear Technology for their professional encouragement, suggestion, technical guidance and support in preparation of this project.

I am grateful to all my lab seniors; Dr. Aris Doyan, Dr. Susilawati, Mr. Ajis Lepit, Mr Hamzah Harun, Mr Asri Teridi, Mr Iskandar Shahrim, Mdm Azlina Baha and Mdm Nuraihan Harun for their assistance, discussion and moral support.

Not forgetting, my great appreciation and special thanks to my mother, Mdm. Sarimah and all my family members Zaifol, Asora, Rosli, Affendi, Azhar, Rosidiah, and Mazidah. I am also greatly indebted to all my friends, especially Azian Othman, Norjannah Azman, Feisal, Walter, Fazlina Mazbah, Maznah Basir, Zuraيداتul Akma, Fatimah Syura, Hafizah Rahim, Hafizah Rais, Hasnita Harun and Imran Bahir for their moral support, cooperation and encouragement and who have been understanding and supportive during my study in Universiti Putra Malaysia.

I certify that an Examination Committee has met on 12 June 2006 to conduct the final examination of Norazimah Mohd Yusof on her Master of Science thesis entitled “Effects of Radiation on Conductivity and Dielectric Properties of Polymehtyl Metha acrylate/Acrylic Acid Polymer Blends” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

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

NORAZIMAH BINTI MOHD YUSOF

Date:

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