SYNTHESIS AND CHARACTERIZATION
OF
POLYAMIDE 6 NANOCOMPOSITE
MEMBRANE

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CHEMICAL ENGINEERING
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Synthesis and Characterization
Of
Polyamide 6 Nanocomposite Membrane

by

Mahathir Mohammad

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

____

(Nor Yuliana Yuhana)
Main Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
Jan 2005

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted for this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been taken or done by un specified sources or persons.

Mahathir Mohammad

ABSTRACT

The usage of polyamide 6 membrane has been used in the separation process industry for decades. In such process, the membrane is exposed to high pressure and temperature condition. Another complication is the process of producing a uniform microporous membrane. Recent improve being researched to improve these membrane are adding nanocomposite filler. This comes to the objectives of this study which is to study, prepare and characterize polyamide 6 nanocomposite membranes. The polymer is prepared by mixing formic acid and polyamide 6 pellets, and lastly mixing montmorillonite as the filler by immersion precipitation process. The microstructure, morphology and mechanical properties of polyamide 6 nanocomposite membrane is being studied using Dynamic Mechanical Analyzer (DMA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). It is found that at 1% wt. of filler, the pore size, numbers of pores and distribution is even across the surface of the membrane. But as the amount of filler increase, the pore size and numbers is reduced even more and distributed unevenly across the surface. From previous study, the T_g increases with the increment of filler amount. The mechanical properties have also improved in terms of storage modulus and yield strength. Finally from XRD, the orientation of arrangement also affect where more filler is added it changes from exfoliated form to intercalated form. As a conclusion, from the SEM results, filler content can influence pore size, their numbers and distribution of pores. Further studies and experiment need to be conducted in order to study the effect of clay on mechanical properties.

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First of all I would like to express my thankfulness to Allah the Almighty who gave me the strength to face the challenges in completing this dissertation to fulfill the Final Year Research Project requirements.

This study would not be possible without the assistance and guidance from key individuals whose contributions have helped in the completion of this research.

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I would like also to acknowledge the cooperation and assistance from Dr. Othman, lecturer from Mechanical Engineering Department for allowing me to use Material Laboratory as well as the equipment in his department. Without his permission, the study of morphology would not have been possible.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Systematic studies on membrane phenomena can be traced to the 18th century philosopher scientists [4]. But no up until 1960s, the usages of membrane as a separation mechanism were used in a few laboratories and small specialized industrial application. This is because at that time, the membrane produced was too unreliable, too slow, too unselective and too expensive. The turning point was made in the early 1960s, of the Loeb-Sourirajan process for making defect-free, high-flux, anisotropic reverse osmosis membranes [4]. Further improvements were made and in the 1980s the first major development in industrial membrane gas separation processes was made. This was in the form of hydrogen separation. Within a few years, Cynara and Separex produce a system that separate carbon dioxide from natural gas [4].

Most gas separation requires that the selective membrane to be extremely thin to achieve economical fluxes [4]. Being produce in such thin profile, there was some problem to the structure of the membranes. The tensile strength and the thermal stability was compromise in such condition. Now research is being made to improve this character but still maintaining the permeability of the membrane. This means that the membranes, with thickness not more than 60μm, would have high mechanical strength that the pores would not break under the pressure exerted to perform gas separation and still maintain high-flux permeability originally obtain for the membrane. The improvement made is done by adding nanoparticles to polymer matrix. The nanoparticles will occupy the spaces in the polymer matrix and improve the properties of the polymer, in terms of mechanical and thermal stability.

1.2 Problem Statement

Preparation of Polyamide 6 membrane by immersion-precipitation method is a challenging task. The successful reproduction of the microporous structure has often been considered as a matter of art [5]. The major difficulty is to control the complex phase separation wherein both crystallization and/or liquid-liquid demixing can occur. The other critical component for preparing a uniform microporous membrane is to

CHAPTER 2

LITERATURE REVIEW

Polyamide 6 has long been used to produce membrane for the purpose of gas separation, mainly in removal of carbon dioxide from natural gas. Just recently improvement was done to the polyamide 6 membrane. By adding clay, specifically montmorillonite, was done in order to improve the properties of polyamide 6.

2.1 Synthetic Membrane

Membrane technology is a vital part of today's process industries. Membranes are widely used in food industry and also automotive industry. Not only membrane provides clean water for billions of people around the The first membrane experiments dated from the 18th century, using membranes (from Latin *membrane*, a thin sheet) of biological origin[15], industrial membrane separation with synthetic membranes has been strongly developed since the introduction of the asymmetric polymeric membrane [15] in the early sixties. Through phase inversion method, synthetic membrane produced has sponge-like inner structure, which contributes to an additional fluid resistance and, a fortiori, a reduced operational product flux at a given transmembrane pressure [15].

Some of the application of these membranes are :

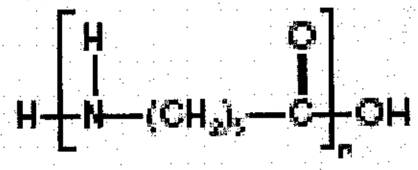
- Separation by charge
- Separation by solution-diffusion process
    - Reverse osmosis
    - Gas separation
    - Pervaporation
- Filtration through size exclusion
    - Molecular sieves
    - Nanofiltration
    - Ultrafiltration and microfiltration

2.2 Polyamide 6

Polyamides are defined as the polymers with the repeating [CO-NH] link unit in the chain.[11] This is the formula the polycondensation reaction of aminocarboxylic acid which is where polyamide 6 falls in:

$$nH_2N(CH_2)_{z-1}COOH \leftrightarrow H - [HN(CH_2)_{z-1}CO]_n - OH + (n-1)H_{2}0$$

Polyamide 6 is produce by heating caprolactam at 250-270°C in an autoclave with water and initiator (aminocaproic acid)[1]. It is a highly crystalline polymer with two crystalline forms, α and γ [7]. The monoclinic α phase is composed of fully extended planar zigzag chain conformation, in which adjacent antiparallel chains are joined to each other by the hydrogen bond. Therefore, it is the thermodynamically most stable crystalline form, and can be obtained by slowly cooling from the melt. The pseudohexaganol γ phase consists of pleated sheets of parallel chains joint by the hydrogen bond. It is less stable and can be obtained by fast cooling from the melt or fiber spinning at a high speed.



$$H-\left[\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n-OH$$

2.3 Montmorillonite

Montmorillonite[(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2·n(H2O)][10] is a clay mineral that consists of stacked silicate sheets whose thickness is approximately1.00nm. Its crystal structure is comprised of two-dimensional layers formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either aluminum or magnesium [6]. Stacking these layers generates van der Waals gaps or galleries. The galleries are occupied by cations, typically sodium and/or calcium ions, which balance the charge deficiency, which is generated by isomorphous substitution within the layers.

Fig1 : Picture size 67 microns.[10]

2.4 Phase Inversion Method

This is one of the methods in order to produce polyamide 6 nanocomposite membrane. Phase inversion (originally introduced by Cestings) is a very versatile technique, in one single process step various type of membranes can be made consisting of a porous support with or without skin layer, where skin layer can be dense or porous with well defined pore size [15]. It is chosen due to the available equipment in the lab. This process consist of the induction of phase separation in a previously homogenous polymer solution either by temperature change, by immersing the solution in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry-process)[3].

CHAPTER 3

METHODOLOGY/PROJECK WORK

3.1 Procedure Identification

Three variables are used as the benchmark.

1. Variation in Montmorillonite Composition

Membrane	Thickness	Dope Composition (wt%)			Nanocomposite Composition (wt%)	
	(μm)	Water	Formic Acid	Polymer	Dope	MMT
N6	30	0	80	20	100	0
N6/MMT-3	30	0	80	20	97	3
N6/MMT-5	30	0	80	20	95	5
N6/MMT-7	30	0	80	20	93	7
N6/MMT-9	30	0	80	20	91	9

These variable was chosen to observe and located whether there will be any significant changes in the membranes compared to the pure polyamide 6 membranes. From these variables we can obtain the best condition in order to produce a good batch of polyamide 6 nanocomposite while producing good result in terms of their properties.

Methods for producing the membrane were drafted based on previous research done [1-11]. None of the previous method was involved with using polyamide 6 in the form of finish product polymer. Most of the researchers used the monomer, caprolactam to produce a solvent polyamide 6(PA6). We on the other hand diluted polyamide 6 polymer in high concentration of formic acid. The ratio of polyamide 6 to formic acid is 20:80. This was also concluded from pervious studies where this ratio provided a more homogenous solution. This polyamide 6/formic acid solution (known as dope from here onwards) is stirred until all of the polyamide 6 has totally dissolved in the acid. Next the nanocomposite membrane is prepared by stirring the dope mixed with montmorillonite (MMT). The ratio of dope to MMT is shown above. The membrane is cast on a ceramic plate using a Gaderner Knife. The thickness of the membrane is 30μm. This was decided after several test using different thickness.

3.2 Equipment Used

Dynamic Mechanical Analyzer (DMA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) will be used to test the membranes. This test will cover the details of the membrane surface, the orientation of the polyamide 6 and montmorillonite matrix and also to indicate the improvement in terms of mechanical properties of the membrane. For DMA, the data that will be obtained is storage modulus (M') and glass transition temperature (T_g). Storage modulus refers to the elasticity of the material, where it measures the amount of force is required to begin elongation of any material at a given temperature. The glass transition temperature refers to the approximate midpoint of the temperature range at which there occurs a break or discontinuity in the curve when molar volume, V is plotted against temperature.[14] The glass transition manifests itself as a tremendous change in viscosity over a small temperature range. SEM shows us the structure of the membrane at nano level, where we can observe the pore sizes, pore dimension and also the distribution across the membrane. XRD shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material.

CHAPTHER 4

RESULTS AND DISCUSSION

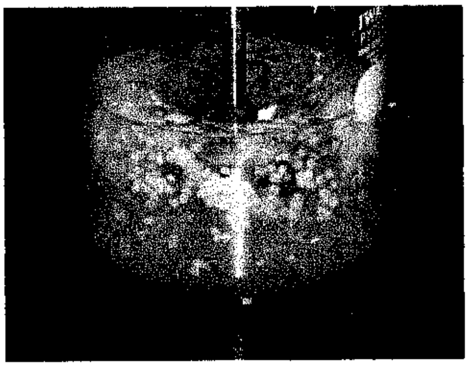


Fig 2: Mixing of Polyamide 6 and Formic Acid

4.1 Sample Preparation

4.1.1 Dope Mixing

The measured amount of PA6 and formic acid is mixed in a beaker and stirred. In order to obtain a homogenous dope, the solution has to be stirred until all of the polyamide 6 dilute in formic acid. It is found that it required more that 1 hour of stirring obtaining 100g of dope. The amount of time increases with the amount of dope needed. Problems occurring were that the PA6 has a tendency of coagulating and sticking to the beaker's wall. During stirring, constant monitoring is need to avoid the PA6 coagulates from hardening because once it hardens; it will be difficult to break it up. Once PA6 is fully dissolved, a cloudy solution is formed (Fig 3, middle).

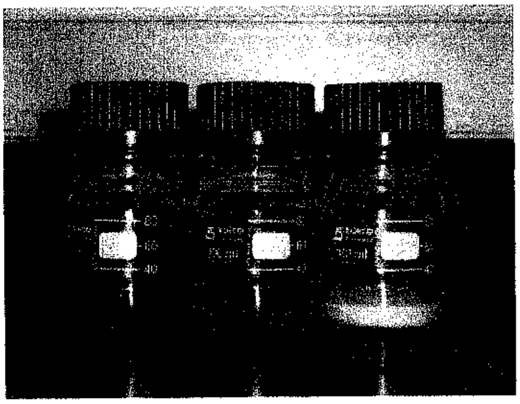


Fig 3: Prepared Dope

4.1.2 Nanocomposite Mixing

Measured and dried cloisite 30B is mixed with the dope at a predetermined ratio. The mixture is stirred. For the initial ratio of 1% MMT it requires almost 2 hours of stirring. This is important in order to be sure that the nanocomposite fills the gaps in the polymer matrix. Another problem identified was that after stirring and the mixture is left idle, the MMT will start to settled forming to layer, which the bottom half is the

MMT and the top half is the dope(Fig 3, Right). Thus, it is required to immediately cast the membrane to avoid the settling for affecting the membrane. Settling occurs overnight for the 1% MMT and takes a longer period as the ratio of MMT increased. Fig 4 shows the prepared nanocomposite mixture (left to right; pure, 1%, 3%, 5%, 7%)

Fig 4: Nanocomposite Mixture

4.1.3 Membrane Casting

The membranes are prepared by using manual casting. Gaderner Knife is used to obtain the desired thickness of the membrane and cast on a ceramic plate. Several values was chosen and tested. 30μm was picked because at that thickness, an even overall thickness was achievable. After the membrane is cast, it is immersed in distilled water remove the membrane from the plate. 2 methods were used in order to dry the membrane. The immersed membrane is hung in an oven at a temperature of 50°C for ½ hour. The second method, the membrane is pressed between 2 ceramic plates at place in the oven at temperature of 80°C for 24 hours. Fig. 5 – Fig.8 are membranes dried at 80°C. It's noted that as the MMT ratio increases, the amount of wavy surface increases. This is most likely due to the movement of water during drying. The reason behind this pattern is still being look in to.

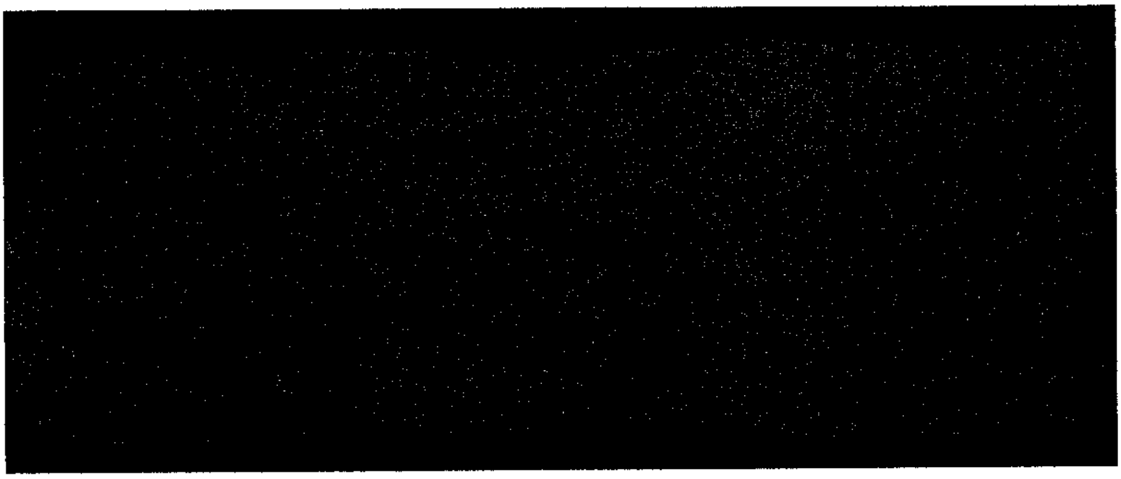


Fig 5: PA6MMT 1% Membrane

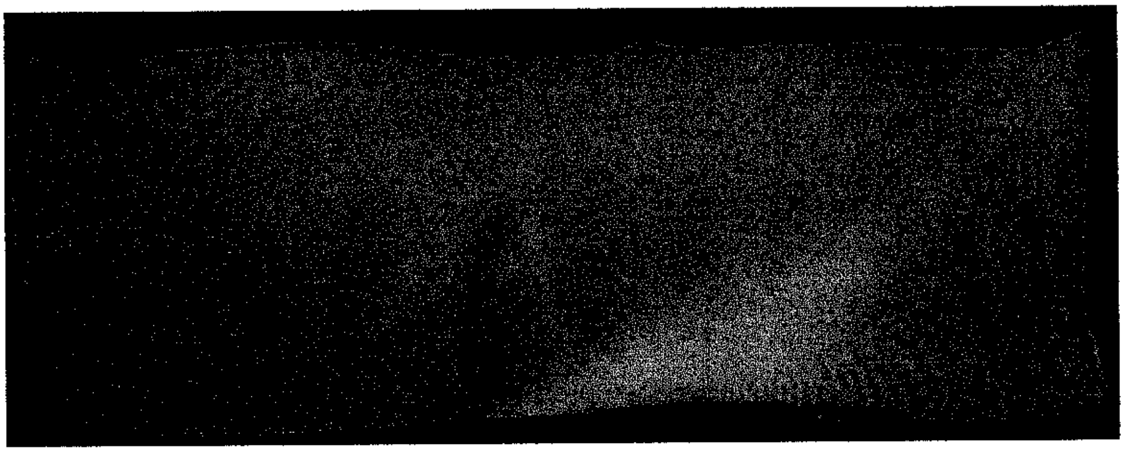


Fig 6: PA6MMT 3% Membrane

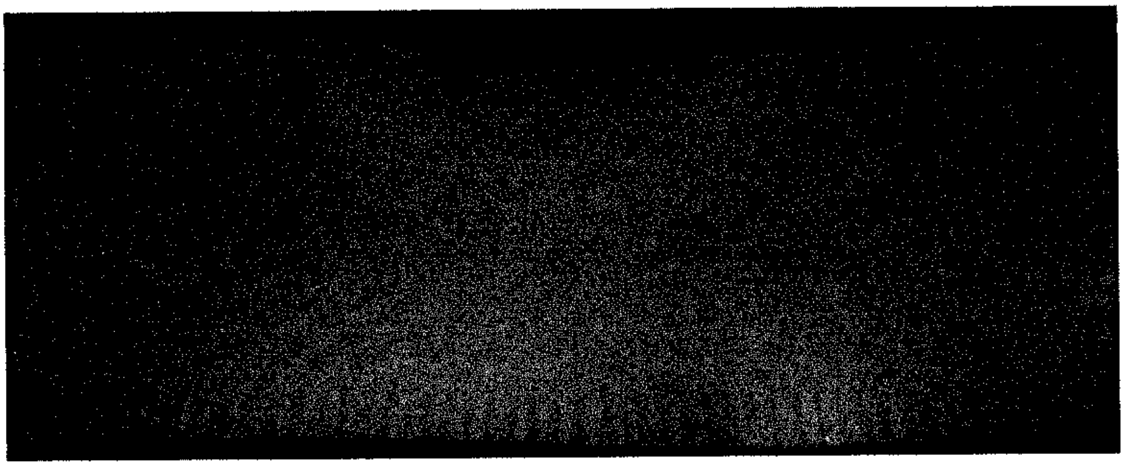


Fig 7: PA6MMT 5% Membrane

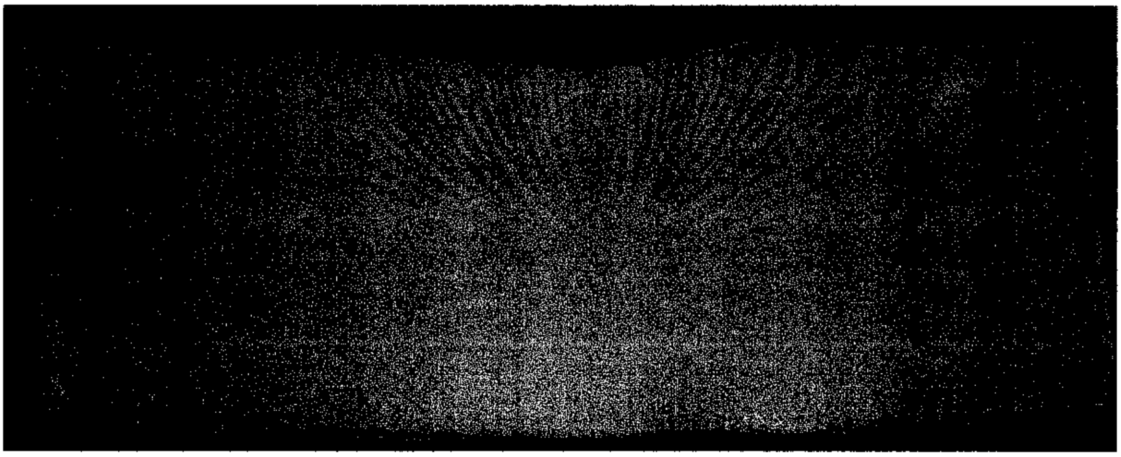


Fig 8: PA6MMT 7% Membrane

4.2 XRD Predicted Patterns

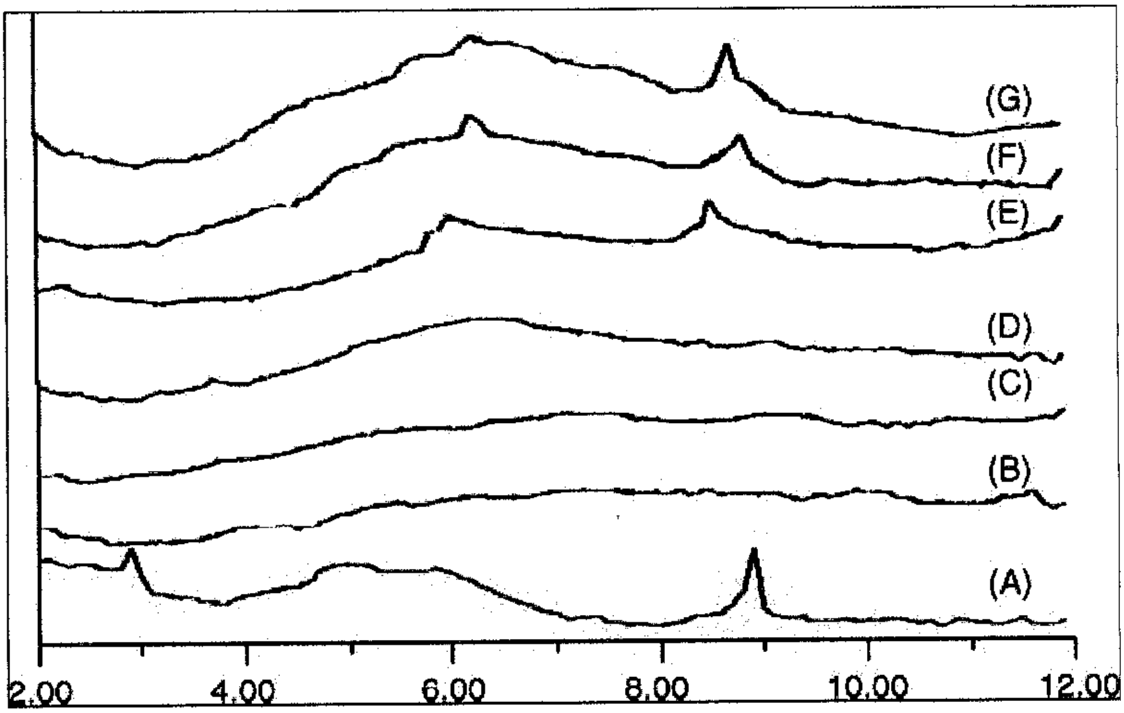
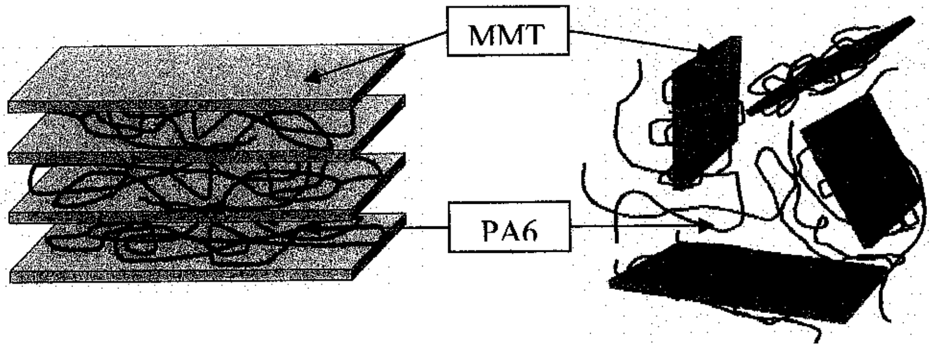


Fig. 9 : X-ray diffraction patterns of the polyamide/SDS–clay nanocomposite membranes: (A) SDS–clay; SDS–clay content: (B) 2 wt.%; (C) 3.5 wt.%; (D) 5 wt.%; (E) 6.5 wt.%; (F) 9 wt.%; (G) 14.5 wt.%.[8]

Due to unavailability of the XRD equipment, a sample result will be used to show what the expected result of this experiment is. The X-ray diffraction pattern of the polyamide/SDS–clay membranes is shown in Fig. 9. The peak observed in the SDS–clay at $2\theta = 8.8^\circ$ ($d = 10.03$ Å) and $2\theta = 2.8^\circ$ ($d = 31.50$ Å) corresponding to the basal spacing in the SDS–clay. When the SDS–clay content was lower than 5 wt.% (Fig. 9B–D), the silicate sheets were exfoliated and dispersed at the molecular level into the polyamide. However, as the SDS–clay content became higher than 6.5 wt.% (Fig. 9E–G), the hybrids showed peaks at $2\theta = 8.4^\circ$ ($d = 14.7$Å) and $2\theta = 6^\circ$ ($d = 15.1$Å) suggesting that a small part of the SDS–clay could not be exfoliated into the polyamide structure and existed in intercalated form.



Intercalated Material

Exfoliated Material

4.3 Scanning Electron Microscopy (SEM)

Top View

By using SEM, a close up top view of the membrane has been obtained. From the figure below (Fig. 10-15), the major differences are the pore sizes. Pure PA6 has the biggest pore size, while PA6MMT 7% has little or almost none. Montmorillonite acts like a filler. It will fill the gaps in the PA6 polymer matrix and reinforce the structure, but at the same time reducing the size of the pores. The clay reinforced the membrane by making the matrix much stiffer, thus increasing the strength of the membrane. To have a well distribution of the clay, a good mixing is need and good mixing takes time. Due to time constraint, the samples are prepared based on sight. Which means if the is no agglomerate in the mixture; it shows that it has homogenously mixed. This is where SEM takes it roles. The pure PA6 is used as a benchmark. Take 1% clay. It has well distributed clay content due to the constant pore size. Starting from 3 % clay onwards, the pore sizes are random. At 5% clay, there are noticeable thick areas which can be indicated as a spot were unmixed PA6 and clay hardened. Finally at 7% clay there are almost no pores. This is evident of poor mixing. That is one of the reasons. Montmorillonite carries a cation charges. During mixing there are possibility that due to static forces between montmorillonite particles it will stick together and agglomerate at a micro or nano level. This will also contribute to the thick wall segments of the pores. Another is that, the surface captured is the bottom section of the membrane. Where is has a more of joined plates rather than pores. Finally it is also probably due to the MMT that has resided in the PA6 membrane pores. This will slow down the precipitation process during in water bath. At the end of the precipitation process, the MMT will clod up the pores and reduces the permeability of the membrane and also indirectly reduce the total area of the pores. To obtain a precise conclusion, a test should be done where we can see the composition of the thick spot (in red rectangle, which are some of the spots) in the membrane wall.

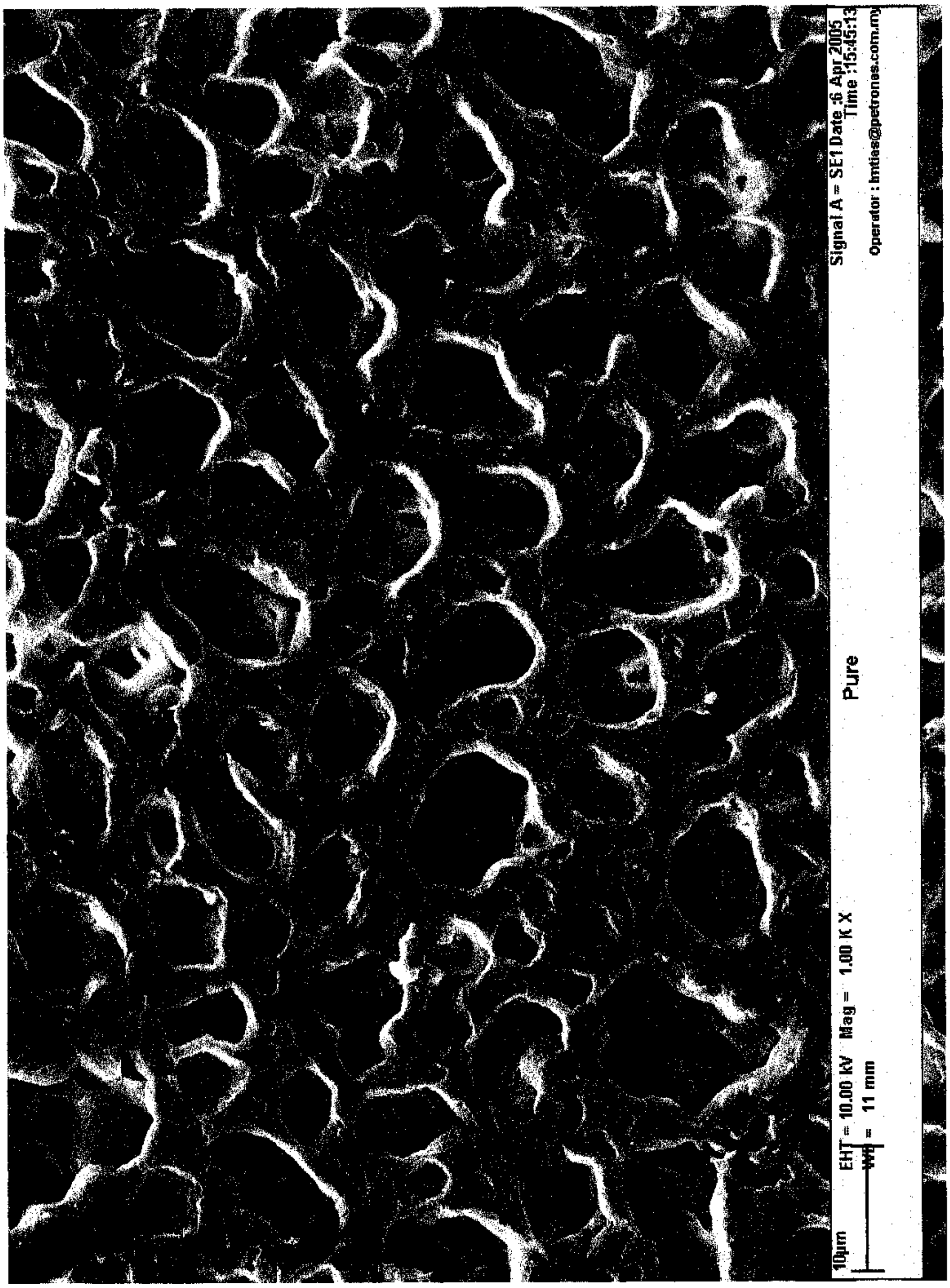


Fig 10: Pure PA 6 (SEM)

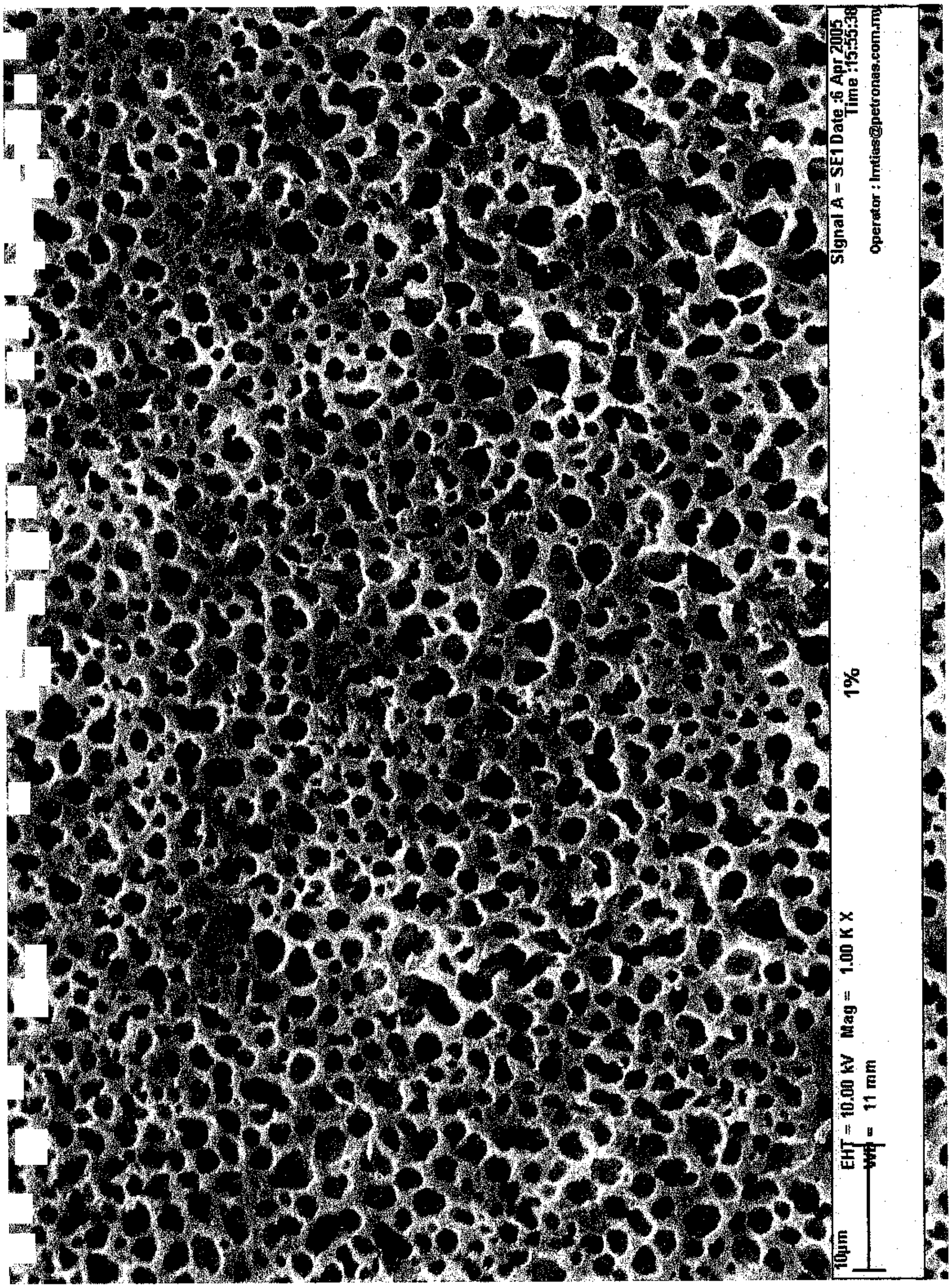


Fig 11: PA6MMT 1% (SEM)

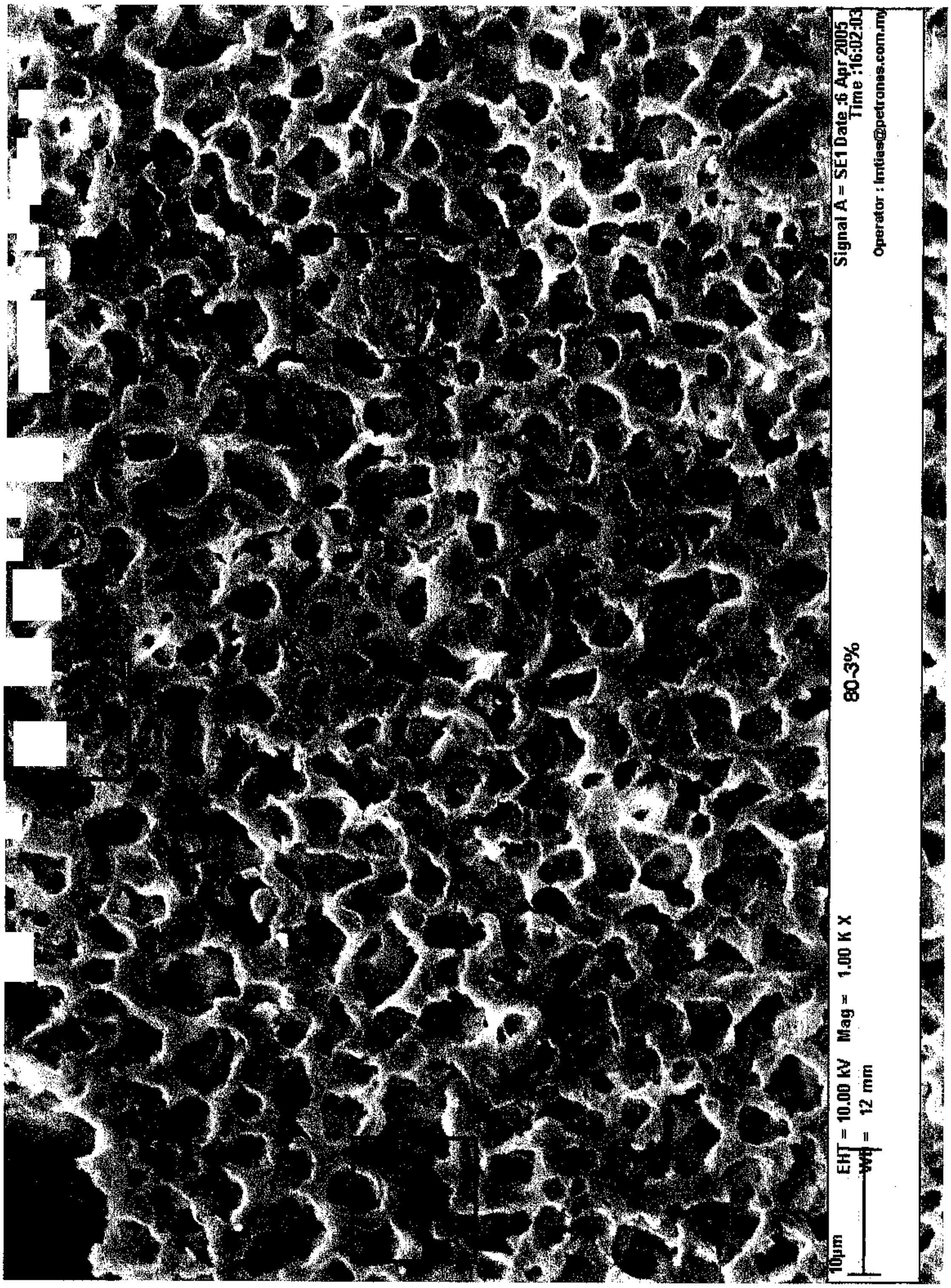


Fig 12: PA6MMT 3% (SEM)

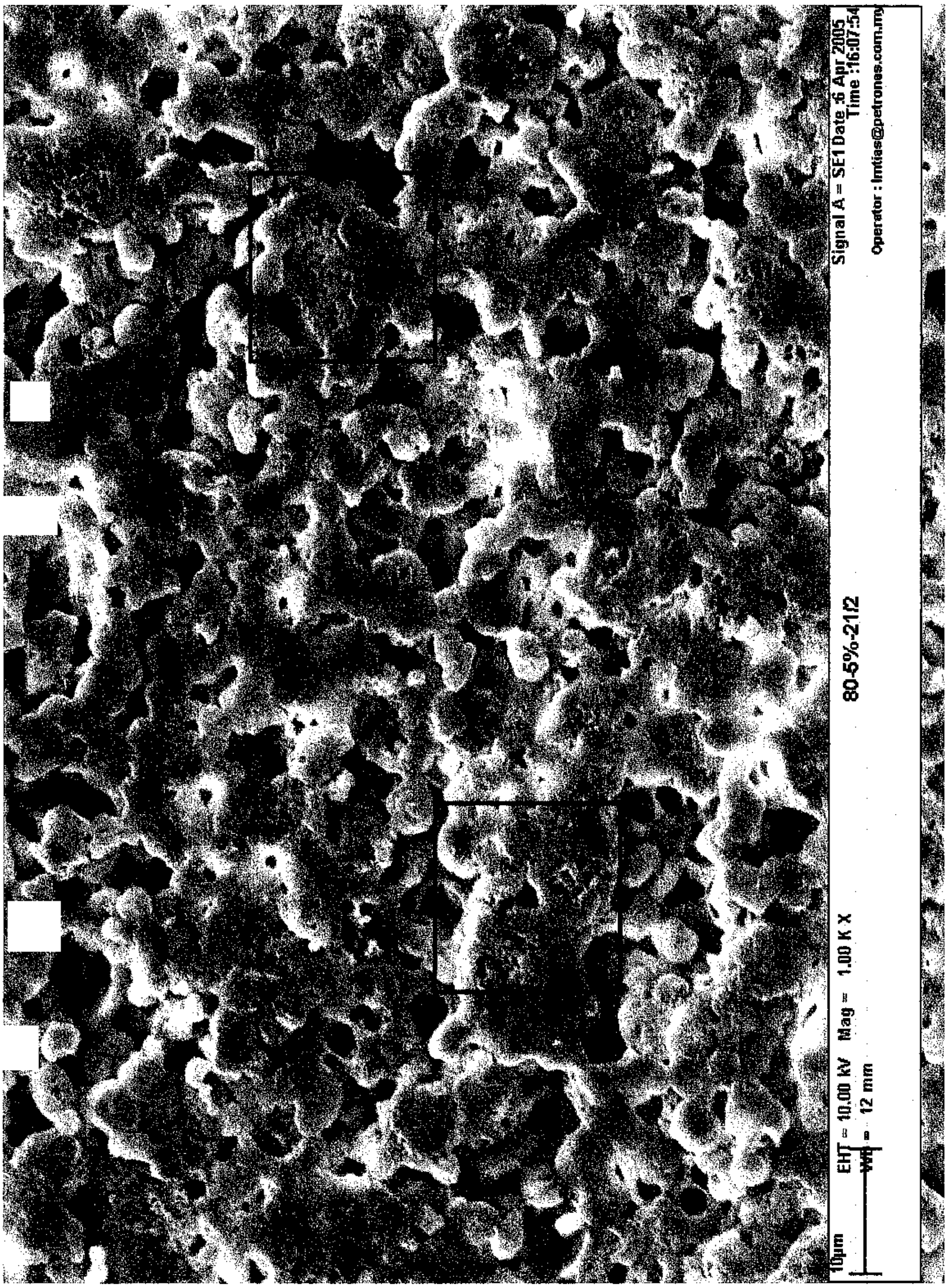


Fig 13: PA6MMT 5%, 2 ½ hours mixing (SEM)

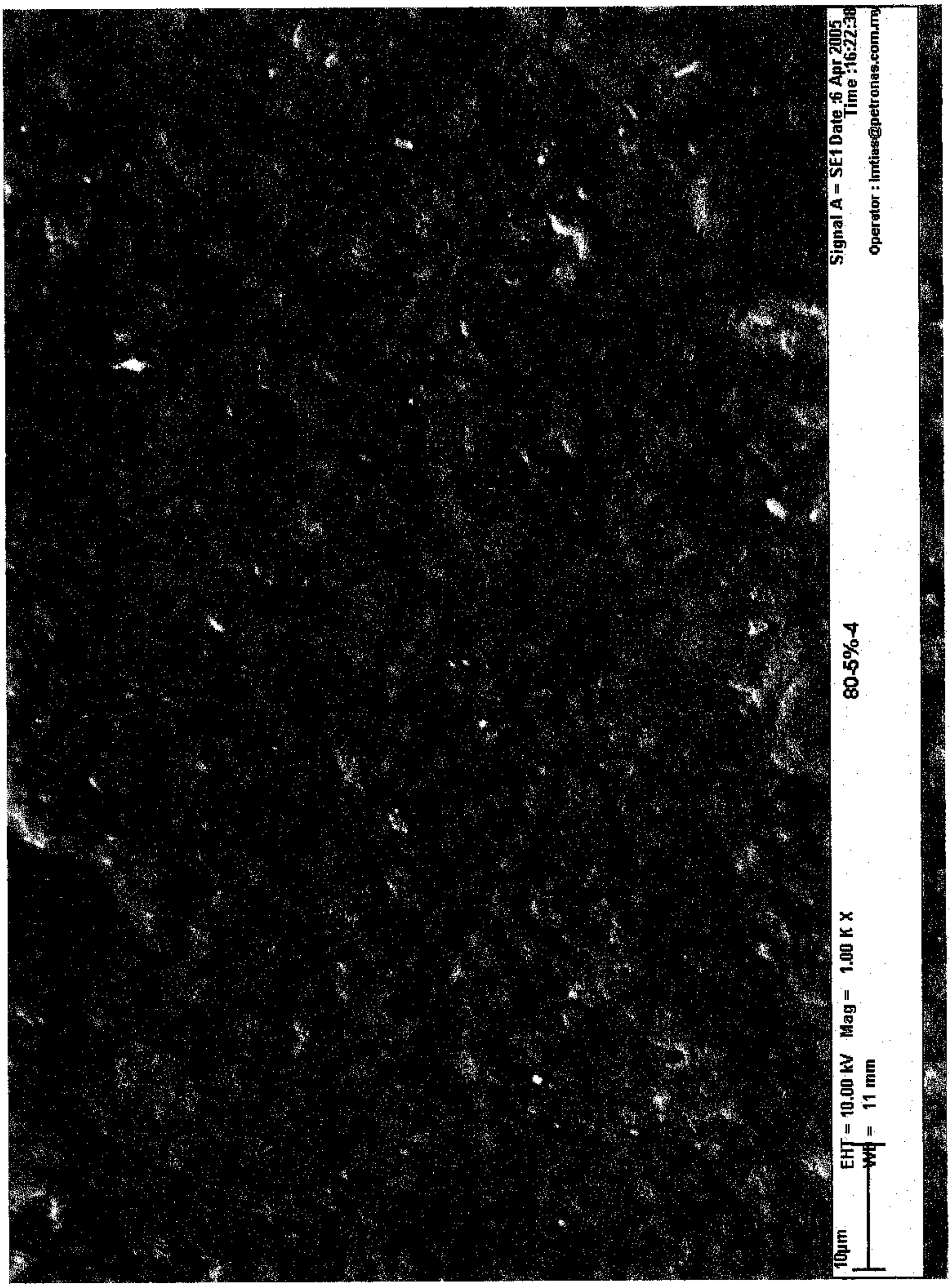


Fig 14: PA6MMT 5%, 4 hours mixing (SEM)

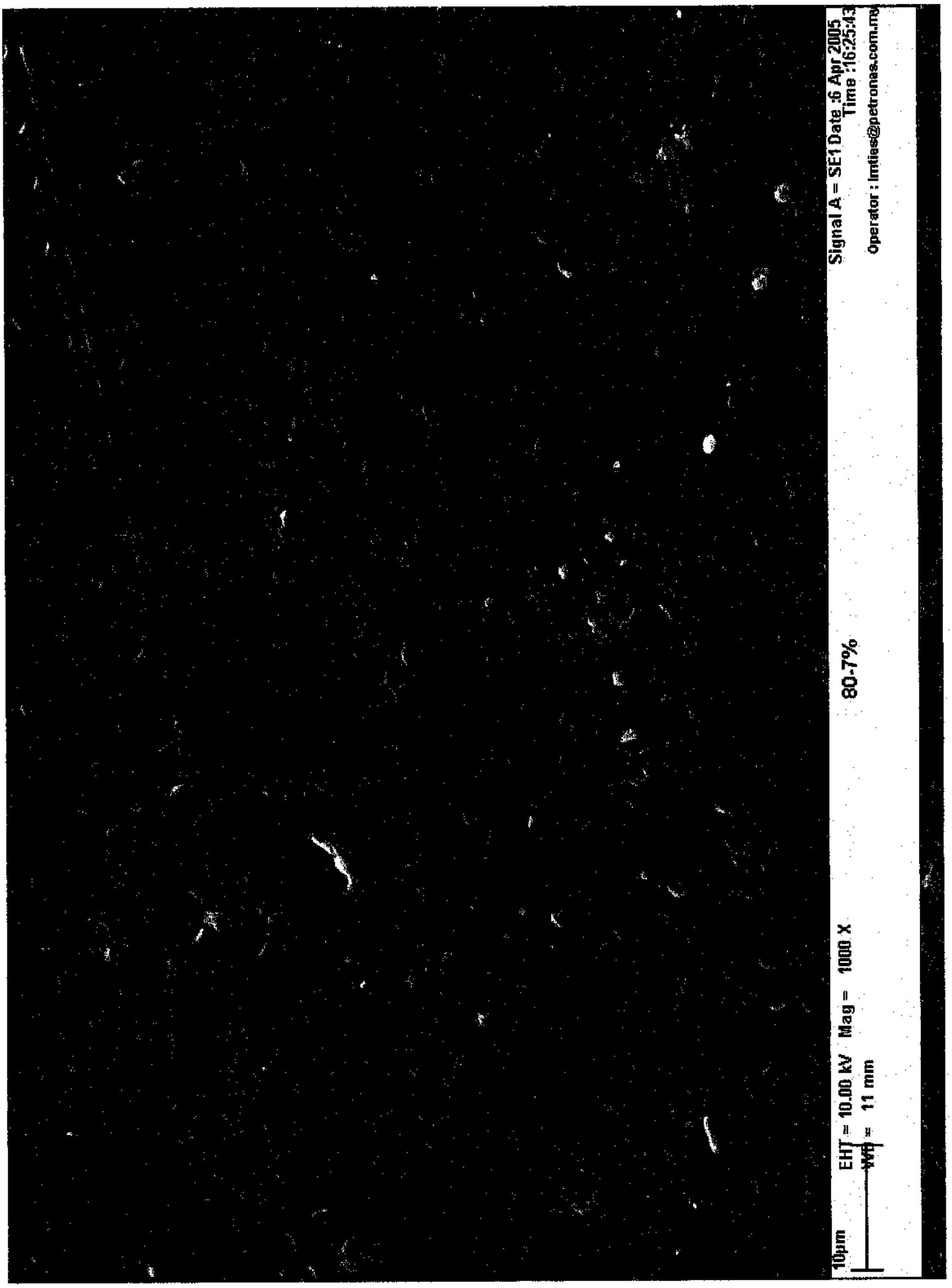


Fig 15: PA6MMT 7% (SEM)

Cross Section View

Using SEM, we've manage to obtain the cross section view of the membrane. But unfortunately we've obtain for pure PA6 (Fig. 16) and PA6MMT 5% 2 ½ mixing (Fig. 17). From the figures, that both consist of a thin dense skin and a cellular bulk. This is ordinarily observed in amorphous membranes that are prepared by immersing-precipitation procedure. Direct comparison is unlikely due to the difference in magnification, but it can be observed that the pore size is much smaller and denser for PA6MMT 5%. It is also observed that the cross section of the wall of the pores of PA6MMT 5% shows that it is much thinner compared to pure PA6.

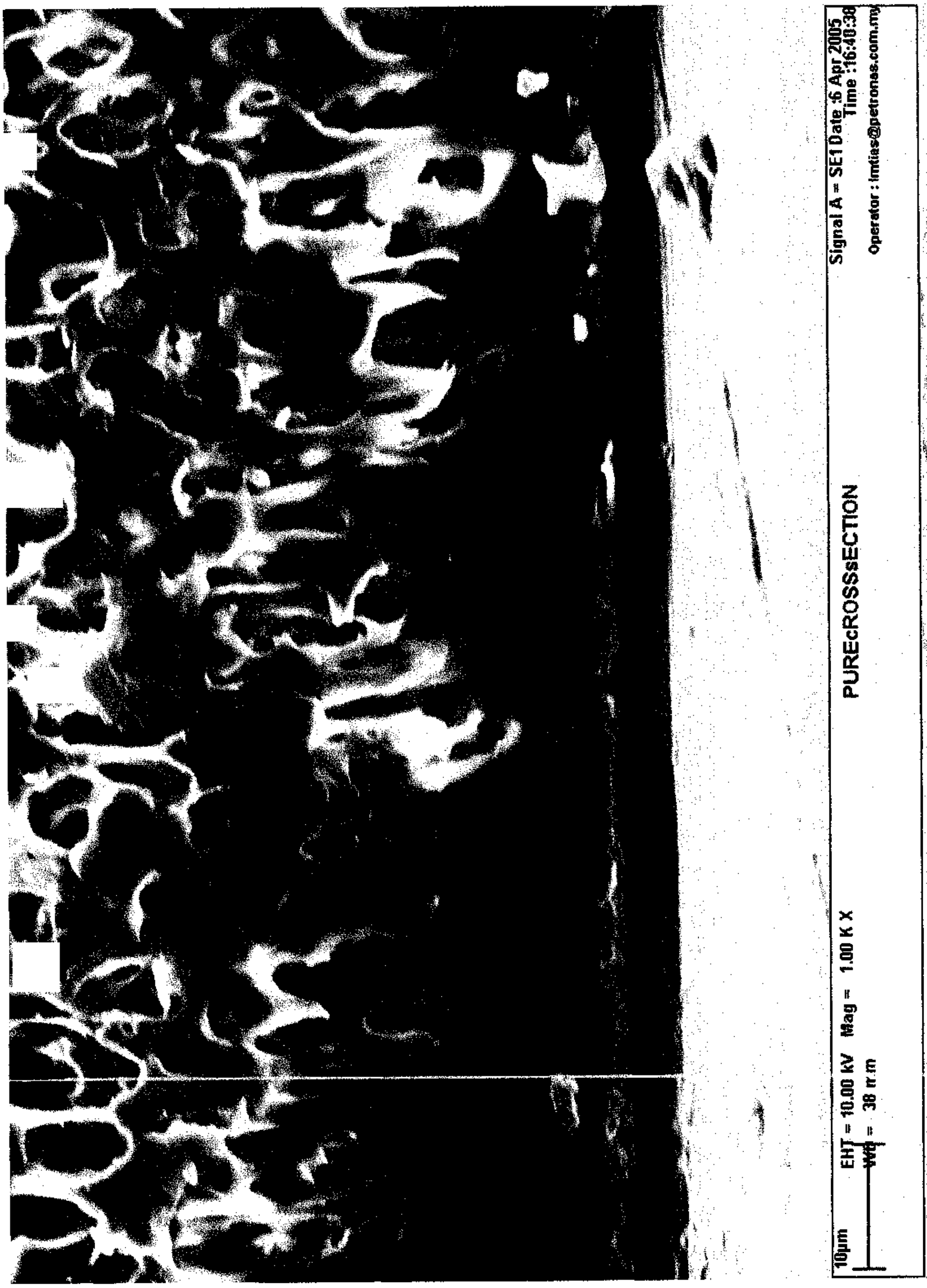


Fig 16: Cross Section Pure PA6 (SEM)

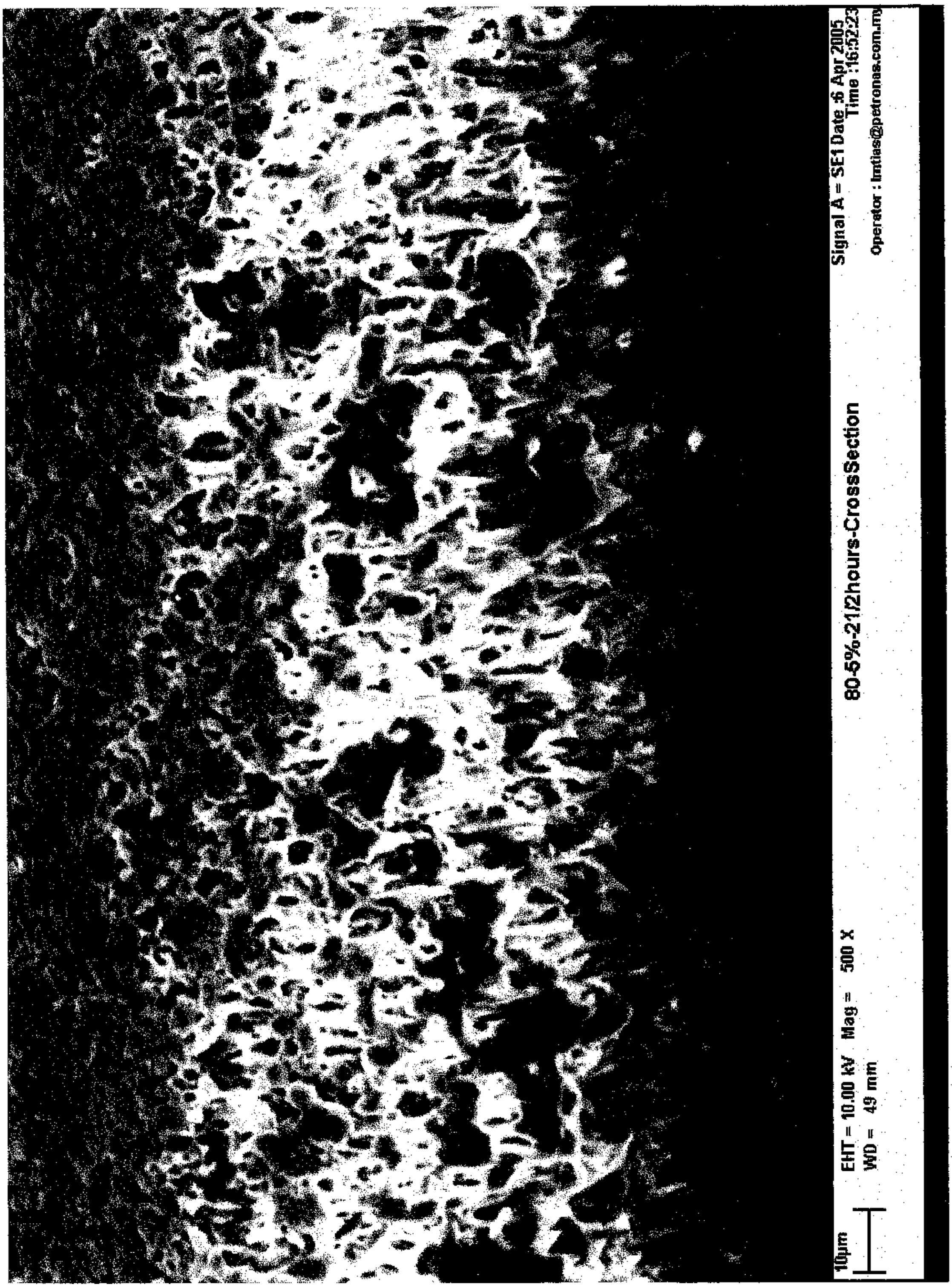
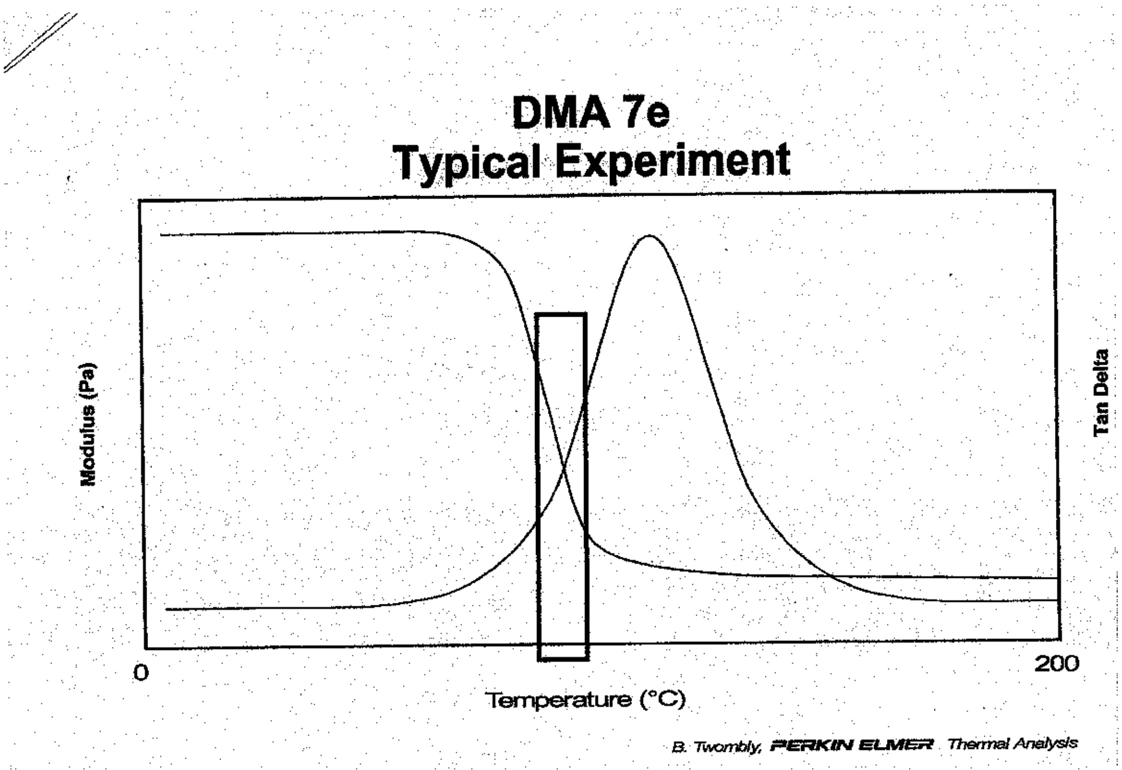


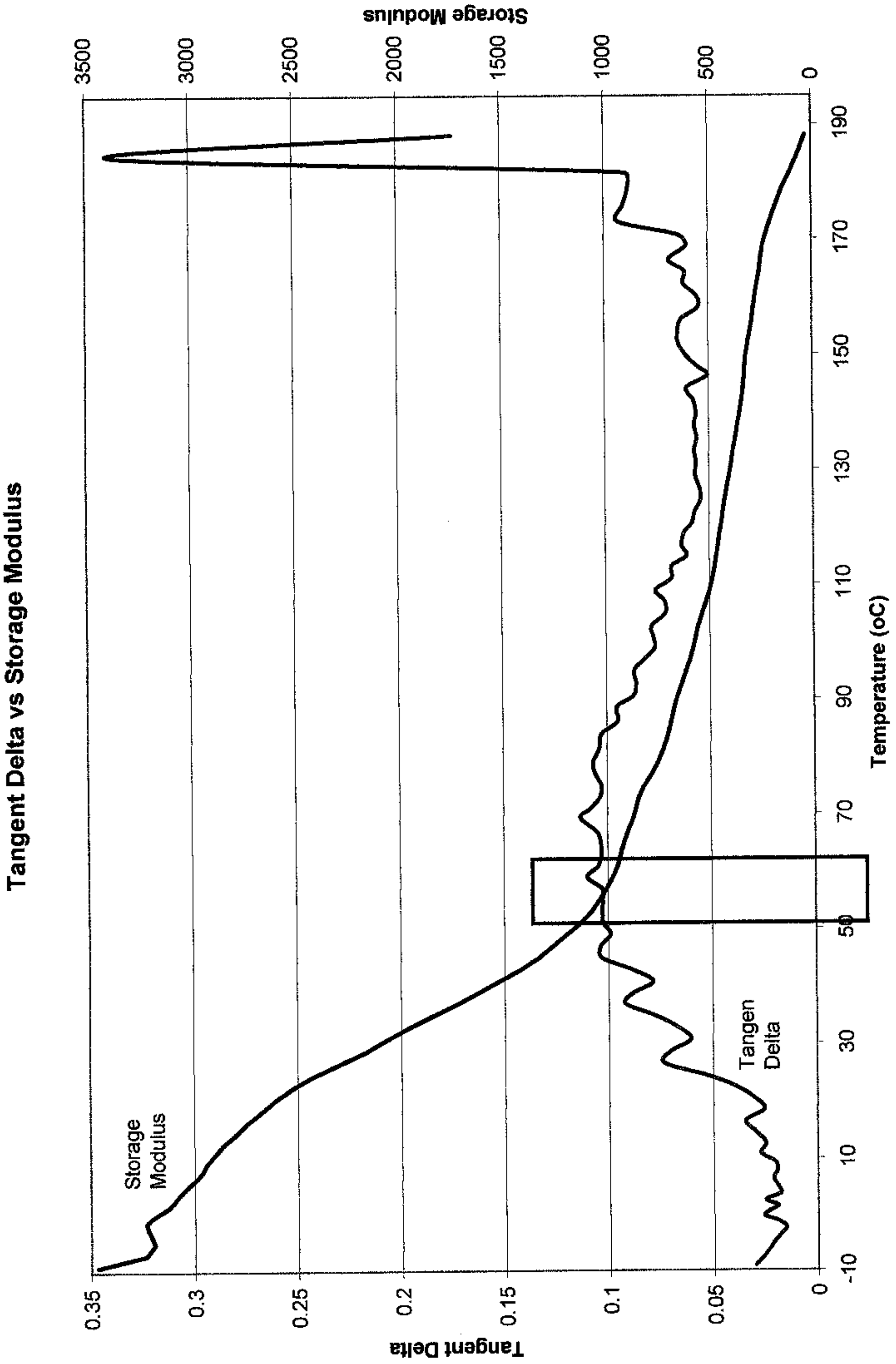
Fig 17: Cross Section PA6MMT 5%, 2 ½ hours mixing (SEM)

4.4 Dynamic Mechanical Analyzer (DMA)

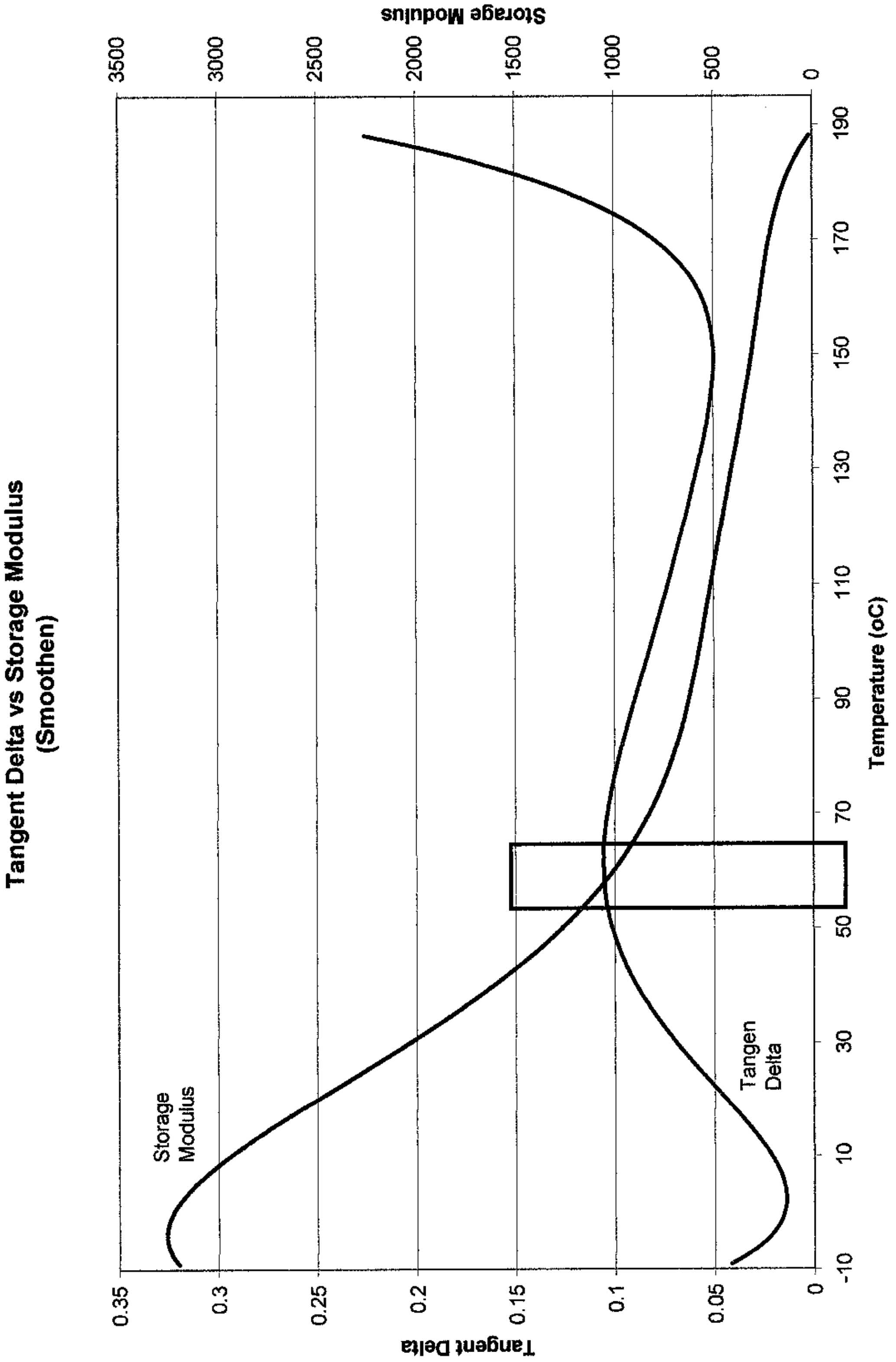


Graph 1: Typical DMA Result

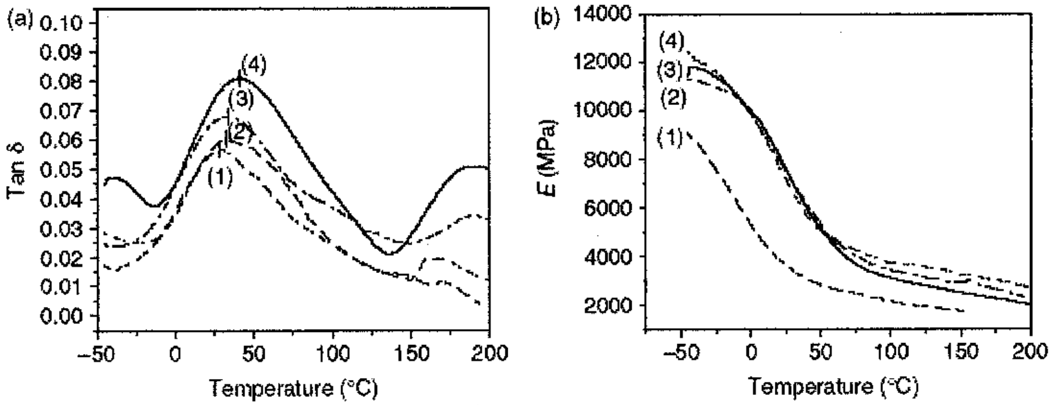
A Dynamic Mechanical Analyzer (DMA) measures changes in mechanical behavior, such as modulus and damping, as a function of temperature, time, frequency, stress or combinations of these parameters. Above is the typical result that can be obtained from a DMA test. For the nanocomposite membrane, stress test is done. In order to see the effect extreme condition has on the membrane, the test was conducted at temperature between -10°C to 200°C. Three result was obtain; storage modulus, loss modulus and tangent delta. The data which will be used for comparison is the storage modulus and tangent delta. Superimposing both graphs, both data will cross at a certain point (represented by blue rectangle in graph 1-3). The temperature range under the graph represents the T_g of the membrane. T_g from the graph is around 50°C to 60°C, almost nearing to value obtain from Differential Scanning Calorimeter (DSC) which is 50°C. Unfortunately, the test result is polluted with noise making the result not 100% accurate. But after several discussion, the result still can be used but not as a proper benchmarking but to observed whether the T_g obtain from DSC.



Graph 2: Tangent Delta vs. Storage Modulus for Pure Polyamide 6 membrane

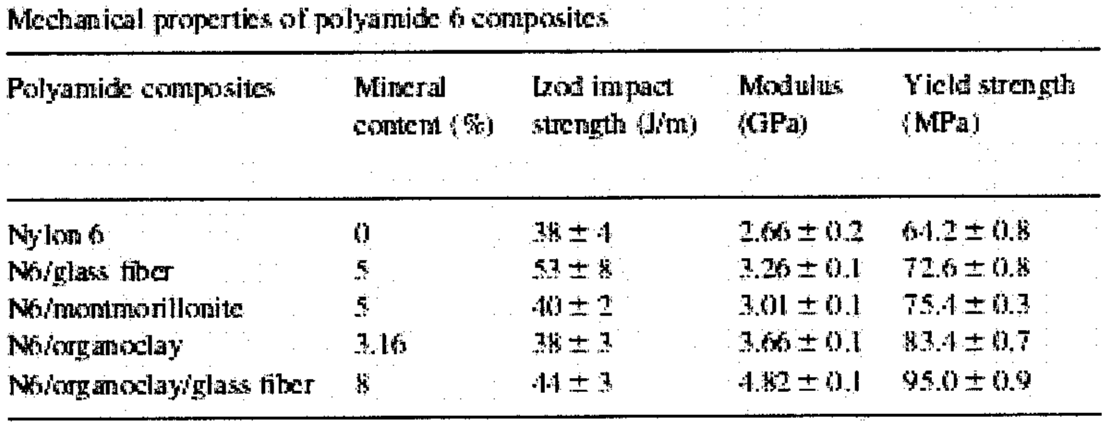


Graph 3: Tangent Delta vs. Storage Modulus(Smoothen) for Pure Polyamide 6 membrane



Graph 4: Dynamic mechanical thermal analysis spectra for (a) tan *δ* and (b) storage modulus $E_{\_}$, as a function of temperature. (1) PA; (2) PA-5; (3) PA-10; (4) PA-5-k [13]

Graph 4 is result obtain for DMA from another research done previously and we should also obtain a similar result is our DMA is in working order. The Dynamic mechanical thermal analysis of polyamide-6 shows an *α*-peak in the tan *δ* curve which originates from the movement of the longer molecular chains in the amorphous region, corresponding the glass transition temperature.[13] The T_g of the PA6MMT shifts to a high temperature as the composition of the MMT increases. It is also noted that the storage modulus decreases with increase in temperature. But still PA6MMT membrane exhibits a higher value compared to pure PA6.



Mechanical properties of polyamide 6 composites

Polyamide composites	Mineral content (%)	Izod impact strength (J/m)	Modulus (GPa)	Yield strength (MPa)
Nylon 6	0	38 ± 4	2.66 ± 0.2	64.2 ± 0.8
N6/glass fiber	5	53 ± 8	3.26 ± 0.1	72.6 ± 0.8
N6/montmorillonite	5	40 ± 2	3.01 ± 0.1	75.4 ± 0.3
N6/organoclay	3.16	38 ± 3	3.66 ± 0.1	83.4 ± 0.7
N6/organoclay/glass fiber	8	44 ± 3	4.82 ± 0.1	95.0 ± 0.9

Table 1: Mechanical Properties [12]

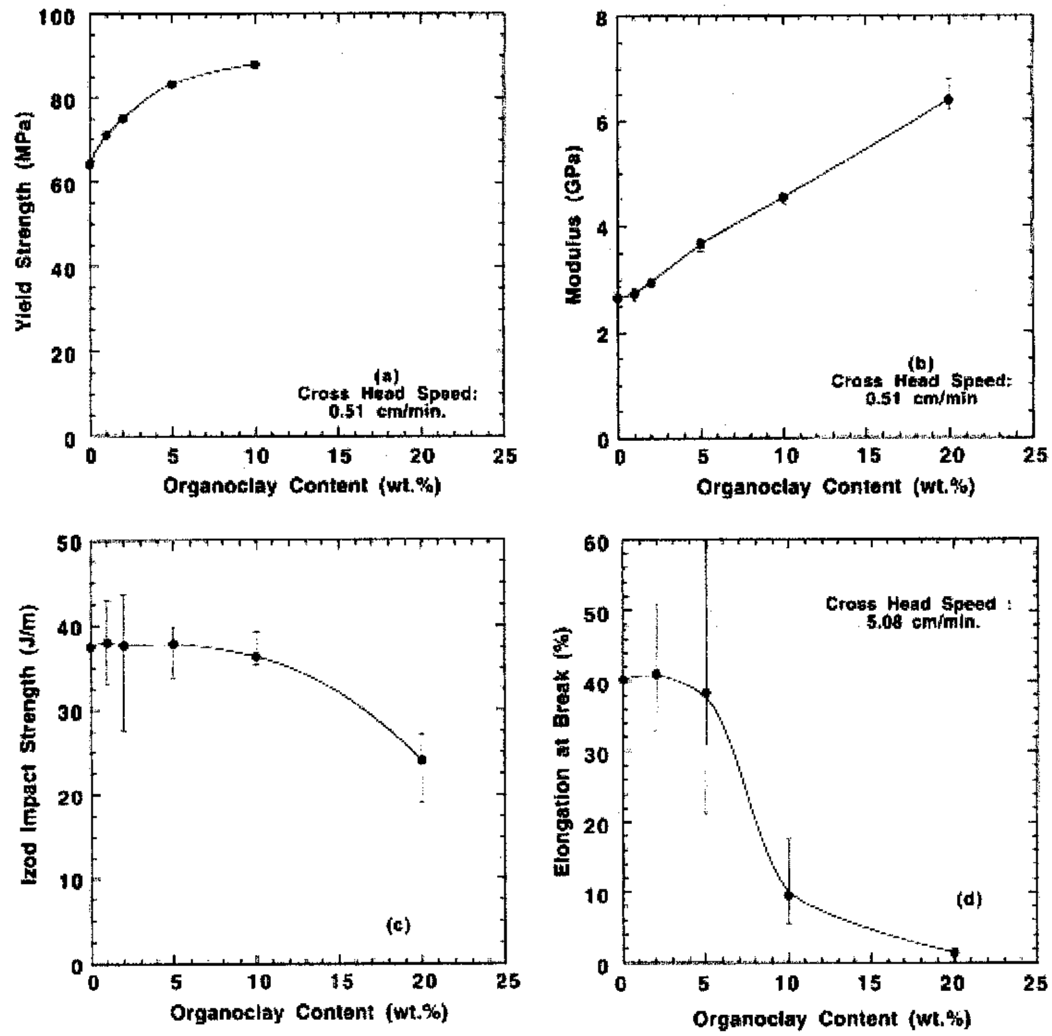


Fig 18: Mechanical properties of melt processed nylon 6/organoclay nanocomposites as a function of organoclay content: (a) yield strength, (b) modulus, (c) Izod impact strength, (d) elongation to break.

Other mechanical test can be done on the membrane. The test results are summarized in Table 1 and Fig. 18 We can see that there is significant improvement in terms of modulus, yield strength and other mechanical properties. This shows that more research should be done in order to further enhance the probability of using nanocomposite to improve any type of polymers used in the industry and enhance the process where the polymers are being used where it is involve with high pressure and high mechanical stress.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The research and experimentation has been done to prepare and characterize of polyamide 6 nanocomposite membrane using montmorillonite as the filler. The samples are then tested and benchmark using Dynamic Mechanical Analyzer (DMA), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and also results from other researchers. This is project has been successfully conducted and the objective reached. We can conclude that:

1. The pore size of the membrane will decrease as the amount of filler is increased.
2. The pore is unevenly distributed as the amount of filler increase.
3. The storage modulus and glass transition temperature improves significantly with increment of filler content.
4. The orientation of the polymer matrix will change from exfoliated form to intercalated form as the amount of filler increase.

Comparison with previous researchers has given good foundation to support the results obtained from this experiment.

5.2 Recommendation

To further improve the results obtained, the sample at same composition should be tested first. This is to determine whether there are other factors that will take role to determine the quality and homogeneously produced membrane. Better equipment used for mixing, heating and drying and casting need to be used in order to obtain more interrelated results from the experiment. DMA, SEM and XRD need to be maintained regularly so that when as testing need to be done, the error won't be so great that will cause the test result to be null.

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