

## Electron Beam Initiated Cross-linking in Hybrid Nylon 66 Membranes

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### ABSTRACT

Electron beam (EB) irradiation at dose of 80 kGy in air has been used as a cross-linking initiator in hybrid nylon 66 membranes to improve the properties and performance of the membrane for separation processes. The cross-linking was characterized by gel content, swelling, scanning electron microscopy (SEM), and thermal stability. Membrane performance was investigated by pure water permeation and by rejection of raffinose and vitamin B12. The results showed that the EB irradiation successfully initiated cross-linking in hybrid nylon 66 membranes.

*Keywords:* Polymer, irradiation, effects, microstructure, thermochemical effects

### 1.0 INTRODUCTION

Increased utilization of electron beam (EB) for the modification and enhancement of polymer properties has been well documented over the past forty years. EB processing has been demonstrated on a large commercial scale to be a very effective method for improving properties of various polymer materials. The EB irradiation can be used for scission of the polymer molecular chain, which subsequently leads to random rupturing of bonds and the cross-linking of polymer molecules. This process results in the formation of large, three-dimensional molecular networks. In practice, chain scission and cross-linking can occur simultaneously, with either mechanism being predominant in some materials [1-3]. This

irradiation also results in significant modifications to the free volume and free volume distribution of the polymer matrix, which has significant impact on the permeability and permselectivity of the irradiated polymer. Various effects can be expected from this process.

Nylon 66, a polyamide (PA) derived from 1,6 hexamethylene diamine and adipic acid, contains a mixture of chains that have either amine or acid groups, or a combination of the two, at their ends. Reports in the literature have shown that the differences in end group configuration can lead to significant differences in the morphology [4-6]. Porous polyamide membrane has been commercialized for many years and is currently widely used in fine-separation processes [7,8].

Study on radiation cross-linking of polyamide 66 (PA 66) or nylon 66 has been reported by several workers [9-10]. Nylon 66 is a typical EB

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irradiation cross-linkable semi crystalline polymer. Cross-linking can change the polymer properties in dramatic ways. For example, cross-linking has been shown to improve thermal properties, change polymer morphology and change the sieving characteristics of polymers.

Modified organic compounds (polymer) containing inorganic substrates have been termed "hybrid materials." In such hybrid materials, advantages found in one component can be used to complement the weaknesses in other components which constitute the hybrid material. Alkoxysilane is one inorganic material that is used to make hybrid materials. The concept of this modification is also to develop new and improved materials for application in the field of membrane science. Xu *et al.* [11] studied surface-modified nano-SiO<sub>2</sub> that was mixed with polyamide 66 by melt processing. Their result indicated that the incorporation of silica nanoparticles decreased crystallization temperature and increased the transition temperature of the composite. Kogure *et al.* [12] prepared an excellent organic-inorganic anion exchange capacity and electro-selectivity membrane by a liquid phase coupling method. Sol-gel is another popular and simple method that is used for the preparation of hybrid membranes. However, this method is not capable of producing good hybrid nylon 66 membranes. Our preliminary study found that the membrane is brittle. In view of this, EB irradiation was used to fabricate high performance membrane. It is known that EB irradiation can improve properties of materials.

In this study, hybrid membrane films were prepared from the polymerization of 3-aminopropyltriethoxysilane (APTES) in nylon 66 with EB as the initiator of reaction. Recently, Tezuka *et al.* (2007) prepared organic-inorganic membranes from 3-aminopropyltriethoxysilane (APTES) and sulfuric acid. They found that the membrane is thermally stable up to 300°C in any composition.

The aim of this research was to investigate the effect of EB irradiation as a cross-linking initiator in hybrid nylon 66 membranes in order to improve the properties and performance of the membrane for separation. The membrane properties were characterized by gel content, degree swelling, scanning electron microscopy (SEM) and

thermogravimetry analysis (TGA). The performance of the membrane for separation was investigated by pure water permeation and by the rejection of raffinose and vitamin B12.

## 2.0 EXPERIMENT

### 2.1 Materials

Additive-free Poly(hexamethylene adipamide) (Nylon 66, product # 42,917-1, pellet form) and 3-aminopropyltriethoxysilane (APTES) (99%) were purchased from Aldrich. Formic acid p.a (FA) (Merck, 99%) was used as the solvent.

### 2.2 Preparation of Membrane and EB Irradiation

Nylon 66 pellets were initially dried in a vacuum oven at 60°C for 4 h and then thoroughly dissolved in the respective solvent at 12.5% concentration polymer (w/w) to form the first solution. APTES was mixed with distilled water and FA (1:4) for 1 h as the second solution. The second solution was dispersed into the first solution under continuous agitation for 3 h (*dope* solution). The final composite solution of nylon 66/APTES had a 90/10 mass ratio and was labeled as H10-0. The homogeneous solution above was left for 24 hours to release air bubbles. A dope solution was uniformly spread on a glass surface using a casting *Gardner* knife as thin films (thickness ca. 350 μm) and then irradiated by electron beam (EB, Alurtron NHV EPS-3000) at an acceleration voltage of 1 MeV and a beam current 10 mA. The irradiation dose was 80 kGy and given in each pass, and the membrane was then labeled as H10-80. The sample designations are given in Table 1.

### 2.3 Characterization

#### 2.3.1 Gel Content

After irradiation, the films were vacuum dried at 80°C for 12 h (43,200 s), and portions of the dried films were weighed. The dried film portions were then immersed in 85% formic acid. Continuous extraction was carried out for 3 days at room

temperature (fresh solvent being added in little amounts every day); gels were collected by filtering through a fritted glass crucible. The percent gel content was calculated using the formula:

$$\% \text{ gel content} = \frac{\text{unextractable fraction}}{\text{irradiated film weight}} \times 100 \quad (1)$$

The results reported are the average of three measurements on three different portions of each film.

### 2.3.2 Degree of Swelling

The swelling of membranes in water was measured by immersing the dried membranes in water for 48 h at room temperature. The membrane was weighed only after the water on the surface of the swollen films was removed with cellulose paper. The dried membranes were obtained by drying at 60°C until they reached a constant weight. The degree of swelling (%S) was defined by Equation (2), where  $W_s$  is the weight of the swollen membranes and  $W_d$  is the dried membrane weight.

$$\%S = \frac{(W_s - W_d)}{W_d} \times 100 \quad (2)$$

### 2.3.3 Morphological Properties

Morphologies of membranes, including top and cross sectional views, were observed by using scanning electron microscopy, or SEM (Oxford Instrument, 7353, England). The cross section of the hybrid membranes was fractured in liquid nitrogen and coated with Au by sputtering.

### 2.3.4 Thermal Gravimetric Analysis

The thermogravimetric data were obtained from thermogravimetry TGA, pyris-1 (Perkin Elmer, USA) performed under dry nitrogen atmosphere at a flow rate of 30 ml/min and a temperature range of 40–600°C at a heating rate of 10°C/min. The samples were ground into a fine powder. The

measurements were taken using 5–8 mg samples. Weight-loss against temperature curves was recorded.

### 2.3.5 Permeation Measurement and Molecular Weight Cut-off

Permeation measurement was carried out with distilled water, and molecular cut-off was determined by the rejection of raffinose and vitamin B12 (uncharged solutions). The solutions containing raffinose and vitamin B12 were prepared with distilled water at 500 ppm and 100 ppm, respectively. The concentrations of the vitamin B12 and raffinose solutions were analyzed using a spectrophotometer (Shimadzu UV-1601PC). These solutions were thermostated at 25°C ± 0.2°C in a water bath for at least one hour before being used in the experiment. The membrane was immersed at least overnight in distilled water before being used in any experimental work. Solute rejection was determined based on  $R_{real}$ , defined by:

$$R_{real} = 1 - \frac{C_p}{C_w} \quad (3)$$

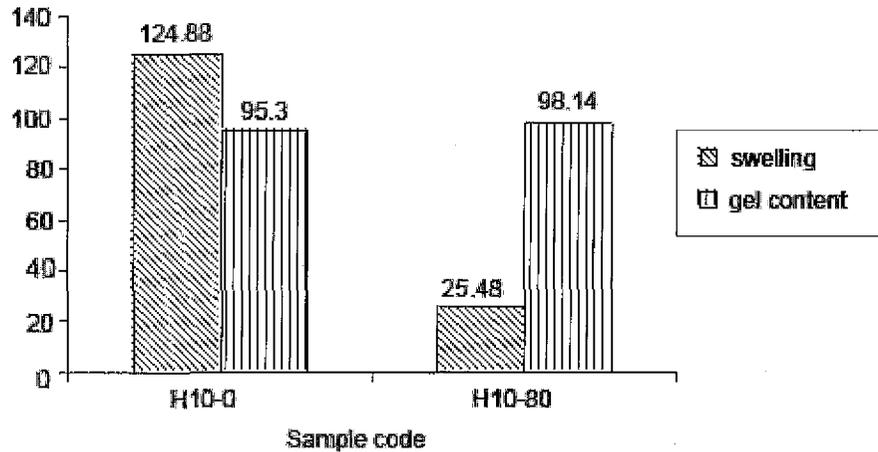
where,  $C_p$  is a concentration of permeate and  $C_w$  is a concentration of feed.

Permeation studies were carried out in an Osmonics SEPA@ST (dead-end) cell. It had a 300 ml volume capacity and effective membrane area of 15.2 cm<sup>2</sup>. The maximum operating pressure of the cell was 450 psig (31 bar). There was a magnetic stirrer assembly inside the cell feed chamber, which allowed for the use of magnetic stir plates for mixing. The stirrer's operating speed was 400 rpm, and the pressure of the experiment was 5–25 bar. Approximately 15 ml of the permeate was collected in a graduated cylinder.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Gel Content and Degree of Swelling

The gel content and degree of swelling analysis were carried out to investigate radiation cross-linking. Figure 1 shows the gel content and degree of swelling of the hybrid membrane nylon 66 before



**Figure 1** Gel content and degree of swelling of the hybrid membrane nylon 66 before and after EB irradiation at 80 kGy

and after EB irradiation at 80 kGy. From Figure 1, it can be seen that EB irradiation at 80 kGy increased the gel content of hybrid nylon 66 and decreased the degree of swelling. These results indicate that the EB irradiation affected the radiation induced cross-linking network. At this dose, the trapped radicals accumulated causing an increase in the probability of recombination and, subsequently, more crosslinkings. The gel corresponds with the network structure in an amorphous region of nylon 66 due to the insolubility of the material. A previous study reported that EB-crosslinking increased gel content [10, 13,14]. Sengupta *et al.* [10] also reported that, below 200 kGy, there is an absence of any gel content. They observed gel content starting at a dose of 200 kGy. Ueno [9] reported that PA 66 irradiated to a dosage of 60 kGy by EB exhibited a gel content of 80%, and, at double the radiation dose, the gel content was only slightly decreased. The relationship between gel content and radiation-induced crosslinking is well described by [2].

From Table 1, it can be seen that the increase of the gel content is not only induced by EB irradiation but also contributed to by APTES. In

our previous work [15] before the addition of APTES, the gel content of nylon 66 only 30.93%. As is well known, APTES is one of the known silane coupling agents.

### 3.2 Scanning Electron Microscopy (SEM)

Figure 2 illustrates the top surface and the cross section of hybrid nylon 66 membrane prepared by sol-gel and EB irradiation. It can be seen that the top surface of the membrane after irradiation exhibited a smooth surface (Figure 2(c)) as compared to before irradiation (Figure 2(a)). The cross section image of unirradiated hybrid membrane is very porous, making this membrane

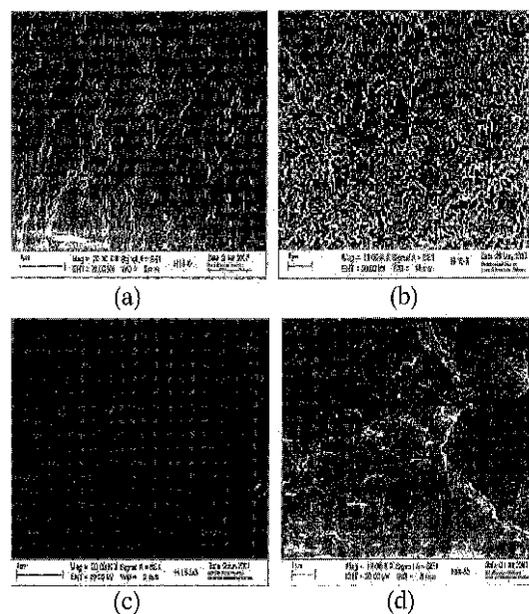
**Table 1** Designation and irradiation dose of dope solution

Sample code	Nylon 66/APTES (part)	Radiation dose (kGy)
H10-0	90/10	0
H10-80	90/10	80

unable to retain pure water and uncharged solute. It is clear from Figure 2 that the top surface of the nylon 66 membranes developed into a dense non-porous skin with EB irradiation. Formation of this dense non-porous skin is due to the sharp increase in interfacial polymer concentration from the EB treatment. Therefore, the top surface of H10-80 membrane is more dense (Figure 2c) and exhibits smaller pore sizes (Figure 2d) when compared to H10-0, making it capable of rejecting raffinose and vitamin B12. The dense membrane was attributed to crosslinking reactions that form a three-dimensional network during the radiation process, and the membrane pore size thus becomes narrower than before irradiation [16]. Krajewska and Olech [16] also reported that crosslinking causes a reduction in pore size. In this study, the crosslinking reaction was supported by gel content and degree of swelling in water data as shown in Figure 1. Crosslinking will cause an increase in gel content and a reduction in the degree of swelling in pure water.

### 3.3 Thermogravimetric Analysis

Thermogravimetric analysis was used to analyze the thermal stability of the material. Thermogravimetric analysis was undertaken on the hybrid nylon 66 membrane in order to determine the effect of EB irradiation on the thermal properties of the hybrid membrane. The thermograms of TGA –DTA are shown in Figs. 3 and 4. These figures show that the temperature of 10% weight loss for the unirradiated hybrid membrane is lower than that for the radiated hybrid membrane, at 352.99 and 422.18<sup>o</sup>C, respectively. This indicates that EB irradiation increased the thermal stability of the hybrid nylon 66 membrane. The unirradiated hybrid nylon 66 membrane has three degradation stages. The temperature of each degradation stage in the hybrids was attributed to scissions of the organic compounds, the end chain (*n*-propyl segment) of the organosiloxanes and the imide segments [17]. The first degradation step of the hybrid membrane is at 173.5<sup>o</sup>C due to the incomplete hydrolysis and condensation reactions and different water and solvent adsorption ability. This was caused by a different organic-inorganic



**Figure 2** SEM of unirradiated hybrid membrane (H10-0), (a) top surface, (b) cross-section and irradiated (H10-80) (c) top surface and (d) cross section

crosslink manner, as previously suggested by [18]. The weight loss of about 27.2% at the onset of degradation of the hybrid membrane is at 384.91<sup>o</sup>C, with the maximum temperature at 423.04<sup>o</sup>C, which occurs at the second degradation stage. According to Tezuka *et al.* [19], the weight loss observed at 400<sup>o</sup>C corresponds to the combustion of organic moieties. The decomposition in the temperature range 400-500<sup>o</sup>C was also ascribed to the decomposition of adhered PA 66 on the silica surface [11]. The last stage occurs at 477.44 <sup>o</sup>C, with a weight loss of 50.7%, corresponding to the decomposition of the main chains of nylon 66.

Irradiated hybrid nylon 66 has only one degradation stage. The onset of degradation is 436.35<sup>o</sup>C at the peak maximum temperature of 480.2 <sup>o</sup>C. This result shows that EB irradiation increased the thermal stability and compatibility of the silane compound in the matrix polymer. Two reasons can be suggested as to why the thermal stability increased in this case. The first reason is due to Si-O-Si linkages in the hybrid membranes,

which increased the degradation temperature by shifting the weight loss to a higher temperature [15, 19]. The second reason is due to the crosslinking of alkyl, amide or amine groups in the irradiated hybrid membrane. These crosslinkages can be based on the crosslinking of alkyl, amine or amide groups in the hybrid membrane or the Si-O-Si covalent bond. This will lead to the initial temperature of weight loss of the irradiated membrane being higher than that of unirradiated membrane, but, above 500°C, the percent of weight loss of H10-80 is higher than H10-0. It is interesting to note that, above 500°C, the weight loss of unirradiated hybrid membrane is lower than that of irradiated membrane. There are some reasons behind this occurrence. One important reason is the presence of the additive in nylon 66 [20]. Radiation effects on the properties of a polymer are difficult to predict, especially in presence of certain additives [21]. Another reason might be due to the crosslink interaction between nylon 66 and APTES, even without the application of radiation. It is known that APTES is one of the silane coupling agents. Silane coupling agents are predominantly used as mediators that bind organic and inorganic materials and also reinforce plastics [22]. These results suggest that the thermal stability of hybrids was enhanced not only by EB irradiation but also by additive behaviour and silica content.

### 3.4 Permeation Measurement

Table 2 shows the permeation study of distilled water. As shown in the second column of the table, the water flux for non irradiated membranes

(H10-0) was not detected, indicating that this membrane did not exhibit water retention capability due to large membrane pore diameters. Crosslinking made the membrane pore sizes narrower than before irradiation. As a result, water fluxes can be detected.

Water permeability of the membrane was determined by the gradient of water flux against pressure. The water permeability of the H10-80 membrane is  $16.84 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ . Based on water permeability, irradiated hybrid nylon 66 at a dose of 80 kGy (H10-80) is of nanofiltration type. The range of water permeability values for nanofiltration membranes that are commercially available is between  $1.33 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$  and  $50.50 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$  [23].

### 3.5 Determination of Molecular Cut-off (MWCO)

Table 2 also shows the membrane solute rejection of vitamin B12 and raffinose at a pressure of 10 bar. As can be seen from this table, the rejection of vitamin B12 (91.87 %) is higher than raffinose (73.34%) for the irradiated membrane. However, there is no rejection by non-irradiated membrane. Solute molecular size is taken into account as the factor in determining the rejection [24]. Vitamin B12 is a larger solute molecule when compared to raffinose, such that vitamin B12 has a higher rejection rate. Rejection occurs in pores smaller than the solute. These smaller pore sizes are due to cross-linking induced by EB irradiation. Membranes having smaller pore sizes exhibit phenomena such as convection and diffusion, which contribute to the separation process.

**Table 2** Membrane permeation at 10 bar

Membrane code	Water flux $10^{-6}$ ( $\text{ms}^{-1}$ )	MWCO (Da)	Rejection (%)	
			Raffinose	Vitamin B 12
H10-0	nd	nd	nd	nd
H10-80	46.79	1355	73.34	91.87

nd = no detected because no water flux was obtained

Generally, these results clearly show that EB irradiation treatment affected the membrane molecular cut-off. The MWCO of the irradiated hybrid membrane is 1355 Da. Based on MWCO and rejection data of uncharged solute (vitamin B12 and raffinose), the irradiated hybrid nylon 66 at a dose of 80 kGy (H10-80) is of nanofiltration type.

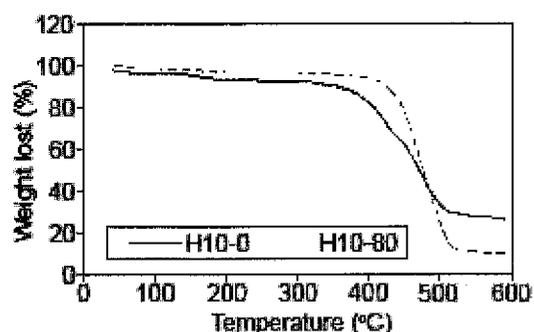


Figure 3 TGA curve of unirradiated (H10-0) and irradiated (H10-80) hybrid membranes

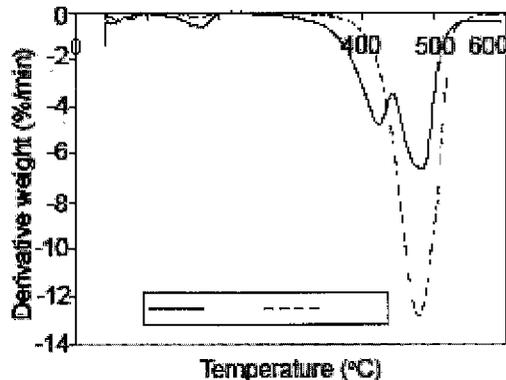


Figure 4 DTA curve of unirradiated (H10-0) and irradiated (H10-80) hybrid membranes

#### 4.0 CONCLUSION

Based on the results from this study, it can be concluded that EB irradiation initiated cross-linking of hybrid nylon 66 membranes. The evidence of crosslinking was demonstrated by an increase of the gel content and decrease of the

degree of swelling. The crosslinking improved the performance of the hybrid membrane. From TGA analysis, it was found that irradiated hybrid membrane has a higher thermal stability than that of unirradiated membrane. Upon irradiation, membrane pore sizes become smaller and rejection of vitamin B 12 is high. Based on water permeability and rejection data of vitamin B12 and raffinose, irradiated hybrid nylon 66 membrane at a dose of 80 kGy (H10-80) is of nanofiltration type.

#### ACKNOWLEDGEMENT

The authors would like to thank the Riau Province Government for scholarship assistance. We would also like to acknowledge EB Alurtron team Malaysian Institute for Nuclear Technology Research (MINT) for the collaboration.

#### REFERENCES

- [1] Chmielewski, A. G., Haji-Sacid, M., 2004. Radiation Technology: Past, Present and Future. *Radiation Physics and Chemistry*. 71: 17-21.
- [2] Charlesby, A. A., 1960. In *Atomic Radiation and Polymers*. London: Pergamon Press. 11: 72.
- [3] Silverman, J., 1977. Basic Concepts of Radiation Processing. *Radiat. Phys. Chem.* 9(1-3): 1- 15.
- [4] Oshinski, A. J., Keskkula, H., Paul, D. R., 1992a. Rubber Toughening of Polyamides with Functionalized Block Copolymers 1. Nylon-6. *Polymer*. 33(2): 268-283.
- [5] Oshinski, A.J., Keskkula, H., Paul, D. R., 1992b. Rubber Toughening of Polyamides with Functionalized Block Copolymers: 2. Nylon-6,6. *Polymer*. 33(2): 284-293.
- [6] Takeda, Y., Keskkula, H., Paul, D. R., 1992. Effect of Polyamide Functionality on the Morphology and Toughness of Blends with a Functionalized Block Copolymer. *Polymer*.

- 33(15): 3173-3181.
- [7] Persson, A., Jonsson, A. S., Zacchi, G., 2003. Transmission of BSA during Cross-flow Microfiltration: Influence of pH and Salt Concentration. *J. Memb. Sci.* 223(1-2): 11-21.
- [8] Castilho, L. R., Anspach, F. B., Deckwer, W.D., 2002. Comparison of Affinity Membranes for Purification of Immunoglobulins. *J. Memb. Sci.* 207(2): 253-264.
- [9] Ueno, K., 1990. The Radiation Cross linking Process and New Products. *Radiation Physics and Chemistry.* 35(1-3): 126-131.
- [10] Sengupta, R., Tikku, V. K., Somani, A. K., Chaki, Tapan, T. K., Bhowmick, A. K., 2005. Electron Beam Irradiated Polyamide-66 Film-II: Mechanical and Dynamical Properties and Water Absorption Behaviour. *Radiation Physics and Chemistry.* 72(6): 751-757.
- [11] Xu, X., Li, B., Lu, H., Zhang, J., Wang, H., 2007. The Interface Structure of Nano-SiO<sub>2</sub>/PA 66 Composites and Its Influence on Material's Mechanical and Thermal Properties. *Applied Surface Science.* 254: 1456-1482.
- [12] Kogure, M., Ohya, H., Paterson, R., Hosaka, M., Kim, J-J., McFadzean, S., 1997. Properties of New Inorganic Membranes Prepared by Metal Alkoxide Methods Part II: New Inorganic-organic Anion-exchange Membranes Prepared by the Modified Metal Alkoxide Methods with Silane Coupling Agents. *J. Memb. Sci.* 126(1): 161-169.
- [13] Djafar, G., Behjat, A., 2001. Radiation Crosslinking of LDPE and HDPE with 5 and 10 MeV Electron Beams. *European Polymer Journal.* 37: 2011-2016.
- [14] Södergård, A., Ekman, K., Stenlund, B., Lassas, A-C., 1996. The Influence of EB-Crosslinking on Barrier Properties of HDPE-mica Composite. *J. App. Polym. Sci.* 59(11): 1709-1714.
- [15] Linggawati A., Mohammad AW, Gazali Z. Modified Surface Properties of Hybrid Nylon 66 Membrane by EB Irradiation, Proceeding of 3<sup>rd</sup> Scientific Conference, Bangi, Malaysia, January, 2008.
- [16] Krajewski, B., Oleich, A., 1996. Pore Structure of Gel Chitosan Membranes. I. Solute Diffusion Measurements. *Polymer Gel Network.* 4(1): 33-43.
- [17] Chakrabarti, K., Kim, S. M., Oh, E. O., Whang, C. M., 2002. Thermal Analysis of Poly(dimethyl-siloxane)-modified Silica Xerogels. *Materials Letters.* 57(1): 192-197.
- [18] Zong, S -H., Li, C-F, Xiao X-F., 2002. Preparation and Characterization of Polyimide-silica Hybrid Membranes on Kieselguhr-mullite Supports. *J. Memb.Sci.* 199(1-2): 53-58.
- [19] Tezuka, T., Tadanaga, K., Ayashi, A., Tatsumisago, M., 2007. Inorganic-organic Hybrid Membranes Prepared from 3-aminopropyltriethoxysilane and Sulfuric Acid as Anhydrous Proton Conductor. *Solid State Ionics.* 178: 705-708.
- [20] Linggawati, A., Mohammad, A. W., Gazali, Z., Preparation of Nylon 66 Membrane by Electron Beam Irradiation: Dynamic Mechanical Properties and Water Absorption Behaviour. Proceeding of Regional Symposium on Chemical engineering. Yogyakarta, Indonesia, December 2007.
- [21] Cleland, M. R., Parks, L. A., Cheng, S., 2003. Applications for Radiation Processing of Materials. *Nuclear Instrument and Methods Physics Research.* B 208: 66-73.
- [22] Jio, C., Wang, Z., Gui, Z., Hu, Y., 2005. Silane Grafting and Crosslinking of Ethylene-octene Copolymer. *European Polymer Journal.* 41: 1204-1211
- [23] Bowen, W. R., Mohammad, A. W., 1998. Characterization and Prediction of Nanofiltration Membrane Performance a General Assessment. *Trans.IChemE.* 76(A): 885-893
- [24] Tsui, E. M., Cheryan, M., 2004. Characteristics of Nanofiltration Membranes in Aqueous Ethanol. *J. Memb.Sci.* 237(1-2): 61-69.