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GRAFTING OF CELLULOSIC PALMITATE-METHYL METHACRYLATE BY ELECTRON BEAM IRRADIATION AND CHARACTERIZATION OF THEIR MEMBRANES MECHANICAL PROPERTIES

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ABSTRACT

GRAFTING OF CELLULOSIC PALMITATE-METHYL METHACRYLATE BY ELECTRON BEAM IRRADIATION AND CHARACTERIZATION OF THEIR MEMBRANES MECHANICAL PROPERTIES. A cellulose derivative membrane, cellulosic palmitate, has been modified to give a better mechanical properties of composite membranes. Modification has been carried out by adding methyl methacrylate (MMA) onto cellulosic palmitate with volume ratio 1:1 and then irradiated by electron beam at dosage of 3, 5, 7, 9, and 10 kGy. The best performance of MMA grafted cellulosic membrane was successfully obtained for irradiation dose at 5 kGy which has a tensile strength of 76,92 Kg/cm^2 (stronger than that of the original cellulosic palmitate membrane up to 75%). This result is supported by FT-IR spectra which showed that grafting methyl methacrylate onto cellulosic palmitate increased the intensity of absorbance of -CH_2- group (1468.47 and 1450.47 cm^{-1}). In addition, there are also strong absorption in region 1068.64 and 1014.56 cm^{-1} which is absorption for C-O-C (ether linkage) between cellulosic palmitate and methyl methacrylate. X-Ray Diffraction and SEM analysis were also revealed that adding of MMA on cellulosic palmitate affected a degree of crystalline and morphology membrane.

Key words : Cellulosic palmitate, Methyl methacrylate, Electron beam, Grafting

ABSTRAK

***GRAFTING* SELULOSIK PALMITAT-METIL METAKRILAT MENGGUNAKAN IRADIASI BERKAS ELEKTRON DAN HASIL KARAKTERISASI SIFAT MEKANIK MEMBRAN**. Membran yang merupakan turunan dari selulosa, yaitu selulosa palmitat, telah dimodifikasi dalam penelitian ini untuk memperoleh sifat mekanik yang unggul dari sebuah komposit membran. Modifikasi ini dilakukan dengan menambahkan metil metakrilat (MMA) kepada selulosa palmitat pada rasio volume 1 : 1, kemudian diiradiasi dengan berkas elektron pada dosis 3 kGy, 5 kGy, 7 kGy, 9 kGy dan 10 kGy. Kinerja terbaik dari membran selulosa yang telah di*grafting* dengan MMA didapat pada dosis iradiasi 5 kGy, yang memiliki kekuatan tarik sebesar 76,92 kg/cm^2 (lebih kuat dari material orisinil sebelum proses *grafting* sebesar 75 %). Hasil ini didukung oleh data spektrum *FT-IR* yang memperlihatkan bahwa proses *grafting* dari MMA kepada selulosa palmitat telah meningkatkan intensitas dari absorbansi gugus -CH_2- (1468,47 cm^{-1} dan 1450,47 cm^{-1}). Selain itu, ditemukan juga absorpsi yang kuat pada daerah 1068,64 cm^{-1} dan 1014,56 cm^{-1} yang merupakan absorpsi dari C-O-C (ikatan eter) antara selulosa palmitat dengan MMA. Analisis *XRD* dan *SEM* juga menunjukkan bahwa penambahan MMA telah menambah sifat kristal dan morfologi dari membran.

Kata kunci : Selulosa palmitat, Metil metakrilat, Berkas elektron, *Grafting*

INTRODUCTION

Modification of natural polymers such as cellulose and its derivatives have been widely carried out in order to enhance their possibilities in industrial application by formation of cellulose esters, grafting and crosslinking with another synthetic monomers [1], and so on. In the application for separation of racemate, cellulosic palmitate membrane was used to separate the racemic mixture of ibuprofen with a very good separation ratio [2]. However cellulosic palmitate membrane has low mechanical strength. Efforts can be done to improve the mechanical properties of cellulose is by adding supporting materials such as methylmethacrylate (MMA) monomer and polymerized by radiation techniques [3].

Radiation techniques that widely used for the modification of polymers is gamma rays and Ultra Violet (UV). Radiation technique using electron beam machine also has been used for long years ago to modify the polymer [4]. Electron beam as a source of radiation is very competitive when compared with gamma rays. The radiation energy utilization efficiency is very high because the electron beam has a lower energy level than that of the gamma rays. With the low energy level it will not damage the irradiated material. Whereas, comparing with the UV polymerization, irradiation by the electron beam does not require initiator.

In this study, preparation will be carried out from blending between cellulosic palmitate with MMA monomer, then irradiated by electron beam at various radiation doses. Mechanical properties of cellulosic palmitate-MMA membrane will be evaluated using tensile strength instrument. Meanwhile, structural characterization will be performed using FT-IR spectroscopy, the membrane morphology by Scanning Electron Microscope (SEM), and degree of crystallization by X-Ray Diffractometer (XRD).

EXPERIMENTAL METHOD

Synthesis

Synthesis of cellulosic palmitate has been carried out by reacting activated cellulose and palmitoyl chloride using mixed solvent of piridine and DMF at 70 ^{o}C for 3 hours. Membrane was casted by blending cellulosic palmitate and MMA monomer with volume ratio 1 : 1 using methylenechloride solvent. Radiation onto membrane was carried out by electron beam machine at total doses 3, 5, 7, 9, and 10 kGy.

Characterization

Characterization of structure and properties of the membrane were carried out by FT-IR spectroscopy, SEM, XRD and tensile strength instrument.

RESULTS AND DISCUSSION

A cellulose derivative membrane, cellulosic palmitate, has been synthezed and grafted with methylmethacrylate by electron beam irradiation. Based on data in Table 1, it is known that cellulosic palmitate-MMA membranes irradiated at doses of 5 and 7 kGy give better tensile strength compared with cellulosic palmitate membrane. This shows that methylmethacrylate has an impact on the increase of

Table 1. Characterization of the irradiated membranes

Characterization of Product			
Membrane	Radiation Dose (KGy)	Tensile Strength (Kg/cm^2)	Crystallinity by XRD (%)
Cellulosic Palmitate	0	69.42	42.39
Cellulosic Palmitate	1	66.25	-
Cellulosic Palmitate-MMA	3	45.15	-
Cellulosic Palmitate-MMA	5	76.92	64.3
Cellulosic Palmitate-MMA	7	72.14	-
Cellulosic Palmitate-MMA	9	63.77	-
Cellulosic Palmitate-MMA	10	63.42	-

membrane's strength. The result of FT-IR analysis (Figure 1) also showed that grafting has occurred between cellulosic palmitate with methylmethacrylate.

At doses of 9 and 10 kGy the tensile strength of the cellulosic palmitate-MMA was lower than cellulosic palmitate membrane. This indicates that both doses of radiation are too high for grafting the membrane, and tend to cause the degradation. This is in accordance

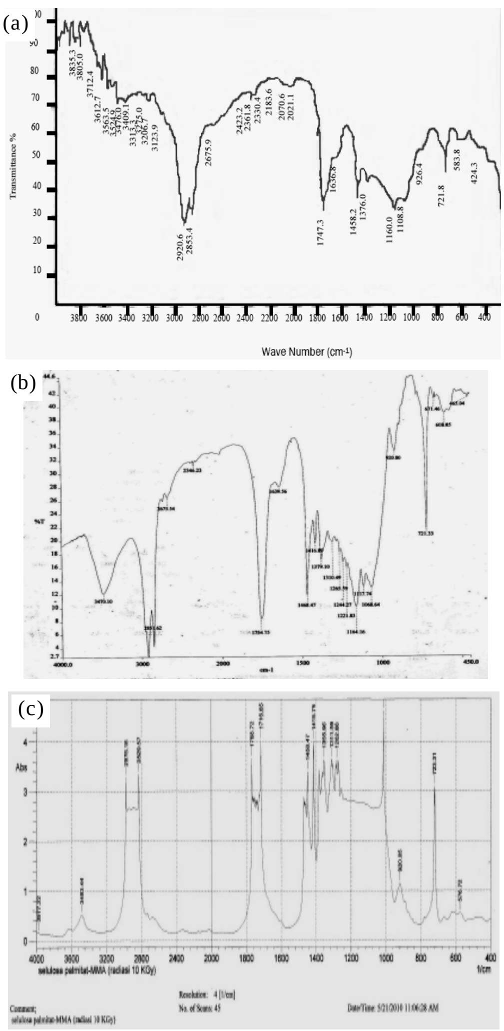

Figure 1. FT-IR spectra of (a). Cellulose palmitate, (b). Cellulose-MMA palmitate 5 kGy radiation dose and (c). Cellulose-MMA Palmitate 10 kGy radiation dose

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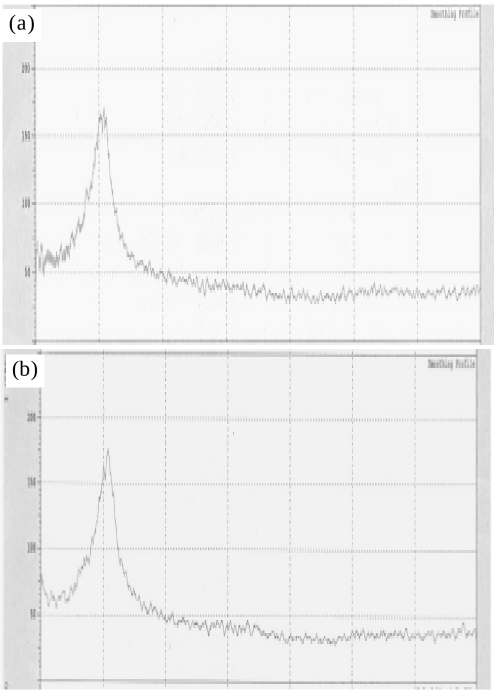

Figure 2. XRD Diffractogram of (a). Cellulosic Palmitate Membrane XRD and (b). Cellulosic Palmitate-MMA Membrane Irradiation by Electron Beam at Doses 5 kGy

with the literature that says that vinyl polymers irradiated with electron beam will experience two types of main reaction, crosslink and degradation. In general, both happen simultaneously, though at high-dose the degradation is more dominant [5]. In addition, the reduction in mechanical strength is affected by the disruption of the crystalline structure of polymers. Grafting of an amorphous polymer on the crystalline region can cause a decrease or an increase of mechanical properties. Grafting which occurs in the amorphous can increase the mechanical properties [1].

Grafting of methylmethacrylate onto cellulosic palmitate increased the intensity of absorbance of $-CH_2-$ group. This can be seen on the irradiated membrane in which the intensity of the absorbance at 1468.47 and 1450.47 cm^{-1} increased. Figure 1 also shows that large doses of radiation can destroy membrane structures. This can be seen from the loss of C-O group absorption peak of the glycoside bond in the membrane which is subjected to doses of 10 kGy. These results are also in accordance with the strength change of membrane due to high radiation dosage as discussed in above.

X-Ray technique also can be used to detect structural changes that occurred due to grafting. Grafting between cellulosic palmitate and MMA produce a higher density and well regulated of polymer structure (crystalline phase). The increase in degree of crystallization as shown in Figure 2, reveals that dose of 5 kGy is the optimum dosage for the occurrence of grafting.

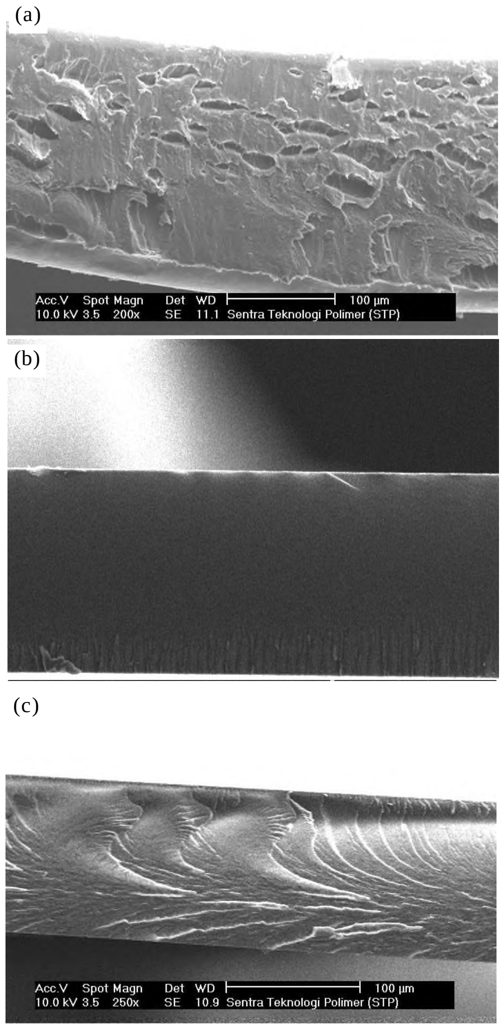

Figure 3. Cross Section imaging of SEM Membrane (a). Cellulosic Palmitate, (b). Cellulosic Palmitate-MMA 5 kGy and (c). Cellulosic Palmitate-MMA 10 kGy

Figure 3 shows the differences in morphology of the three membranes. Cellulosic palmitate-MMA membrane with irradiation dose of 5 kGy (Figure 3(b)) has a tighter structure than that of the cellulosic palmitate membrane (Figure 3(a)) and cellulosic palmitate-MMA membrane with dose of 10 kGy (Figure 3(c)). Therefore, the cellulosic palmitate-MMA membrane with irradiation dose of 5 kGy has greater tensile strength than that of the four other membranes as well as the cellulose palmitate membrane.

CONCLUSIONS

From the above results it can be concluded that, cellulosic palmitate has been succesfully to be blended with methylmethacrylate at the a volume ratio of 1 : 1 using methylenechloride solvent at room temperature. Irradiation by electron beam could cause grafting reaction of cellulosic palmitate membranes with methylmethacrylate or degradation. The optimum radiation dose for the occurrence of grafting was 5 kGy. Grafting that occurs between cellulosic palmitate with methylmethacrylate increased the mechanical properties of membrane. The degradation of the structure was found when the membranes were irradiated by a high dosage result in the decrease of the mechanical strength.

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