

Grafting of Poly(2-hydroxyethyl methacrylate) on Natural Rubber (NR-g-PHEMA): Characterizations and Water Sorption Selectivity of NR-g-PHEMA Membranes

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ABSTRACT

Poly(2-hydroxyethyl methacrylate) (PHEMA) was grafted onto NR latex particles employing emulsion polymerization technique. Grafting efficiency (%GE) of PHEMA on NR particles was found to increase with increasing 2-hydroxyethyl methacrylate monomer (HEMA). Differently, %GE increased rapidly at low initiator concentrations before leveling off at higher concentrations. The NR-g-PHEMA latex was cast into a thin membranes. The membranes were subjected to the tensile testing. The Young's modulus of NR-g-PHEMA membrane was found to improved as %GE increased in contrast to the elongation at break. Revealing by DSC, the states of water in the NR-g-PHEMA membranes appeared as the free water and non-freezing bound water and both increased with %GE. Swelling behavior of NR-g-PHEMA membranes in water-acetone mixtures was investigated. The membrane swelling showed a non-ideal behavior where a maximum swelling degree was found at certain concentrations of water-acetone mixtures. The water sorption selectivity of the membranes was enhanced when increasing %GE for low water content in the water-acetone mixtures. However, as increasing water content, the water sorption selectivity was declined.

Keywords: Grafting, poly(2-hydroxyethyl methacrylate), natural rubber, membranes

1.0 INTRODUCTION

Pervaporation (PV) is an attractive membrane separation process for azeotropic mixtures and close-boiling point components because the separation efficiency does not depend upon the vapor-liquid thermodynamic equilibrium but rather relies on the capability of the membrane to specifically absorb (solubility) the separated specie and allow it to transport through the membrane layer (diffusivity). To limit the swelling and hence impart the water selectivity, the membranes consist of hydrophilic polymer and hydrophobic elastomer could be applied for the separation of organic-water mixtures [1-3]. Generally, the hydrophilic

polymer provides active interactions with water molecules while the elastomeric polymer restrains the membrane swelling as well as improves the integrity of the membrane. Since the phase separate is inevitable for a blend of hydrophilic and hydrophobic polymer, the copolymerization e.g. graft copolymerization [4] could be employed to improve polymer miscibility.

In present study, the graft copolymer of poly(2-hydroxyethyl methacrylate) (PHEMA) and natural rubber (NR) were prepared and the water sorption selectivity was examined. Owing to the presence of hydroxyl group on polymer chain, PHEMA will promote the membrane hydrophilicity. On the other hand, the hydrophobic natural rubber (NR) is selected due to its elastomeric property at room temperature ($T_g \sim -70^\circ\text{C}$) which accommodate the integrity of membranes.

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2.0 METHODS/THEORY

2.1 Synthesis of NR-g-PHEMA Latex Particles

10 g of natural rubber latex (60 wt% dry rubber content) was charged into 100 mL two-neck round bottom flask along with 0.05 g of surfactant sodium lauryl sulfate (SLS), 0.5 g of buffer and 20 g of deionized (DI) water. The mixture was stirred and heated to 60°C under nitrogen atmosphere. The initiator potassium persulfate (KPS) was dissolved in 20 mL DI water before added into the reactor flask. Desired amount of HEMA was diluted with 20 mL DI water before being added into the reactor. The polymerization was carried on for 24 hrs at 60°C with constant stirring under nitrogen atmosphere. The resultant latex was coagulated. The coagulum was washed several times with DI water then dried in the oven at 60°C and weighed. The homo-PHEMA (ungrafted) was extracted using soxhlet-extraction with ethanol. The conversion of HEMA and the efficiency of PHEMA grafting on natural rubber (%GE) were determined by the following equations

$$\% \text{conversion} = \frac{W_G + W_H}{\text{weight of HEMA}} \times 100 \quad (1)$$

$$\% \text{GE} = \frac{W_G}{(W_G + W_H)} \times 100 \quad (2)$$

Where W_G and W_H are weight of grafted-PHEMA and homo-PHEMA, respectively.

2.2 Membrane Characterizations

2.2.1 FT-IR

Infrared spectroscopy of NR-g-PHEMA membranes were performed with Perkin-Elmer FT-IR spectrometer (spectrum one) measuring in the range of 4000-450 cm^{-1} .

2.3 Mechanical Property

NR-g-PHEMA membranes were subjected to the tensile testing following ASTM D412-C standard. The universal testing Machine Lloyd instruments UK model LR 50K was employed. The extension speed of the instrument was 20 mm/min.

2.2.3 States of Water in Membranes

NR-g-PHEMA membrane was immersed in DI water for 48 hrs. Then the sample was placed in a sealed aluminum pan and analyzed by Perkin-Elmer Differential Scanning Calorimeter (DSC) (Pyris 1) heating from -40°C to 40°C with heating rate of 5°C/min. The amount of free water (M_{free}) was estimated from

$$M_{\text{free}} = \frac{\Delta H}{Q} \quad (3)$$

Where ΔH is obtained from the area under endothermic peak at 0°C and Q is the melting enthalpy of pure water which is 334 kJ/kg [5]. Amount of bound water (M_{bound}) was obtained from the difference between the amount of total water absorbed in membranes (M_{total}) and the amount of free water [5].

2.2.4 Swelling Measurement

Dry membrane was first weighed (W_d) then immersed in liquids; immersed in water-acetone mixtures at various concentrations for 48 hrs. Later it was removed from the liquid solutions and wiped with a filter paper to remove the superfluous liquid on the membrane surface then weighed (W_s). The membrane swelling degree (SD) was calculated from the following expression

$$\% \text{SD} = \frac{W_s - W_d}{W_d} \times 100 \quad (4)$$

From the swelling degree, the interaction parameters between pure components (water and acetone) and membranes were estimated employing the Flory-Huggins theory [6]. According to the theory, the free energy of mixing (ΔG) of a binary mixture was expressed as

$$\frac{\Delta G}{RT} = \ln \phi_s + \phi_p + \chi_{ip} (\phi_p)^2 \quad (5)$$

Where R is the gas constant, T is the absolute temperatures, ϕ_s is the volume fraction of the solvent in the polymer and ϕ_p is the volume fraction of the polymer. At equilibrium, the energy of mixing is zero and the binary interaction parameter χ_{ip} can be calculated accordingly

$$\chi_{ip} = \frac{-(\ln \phi_s + \phi_p)}{(\phi_p)^2} \quad (6)$$

If the affinity between the polymer and solvent increases, the amount of liquid inside the polymer will increase and χ_{ip} will be decreased [7].

2.2.5 Sorption Study

NR-g-PHEMA membrane was immersed in known concentration of water-acetone mixtures and allowed to equilibrate for 48 hrs at room temperature. The retaining liquid in the membrane was removed by desorption using a vacuum evaporation method with the apparatus shown in Figure 1. The swollen membrane was placed in a sealed glass tube connected to a cool trap and a vacuum pump. Then the tube was heated at 60°C

for 2 hrs. The composition of the retained-solution was determined by refractive index detector (Waters 2414). The sorption selectivity (α_s) was calculated by:

$$\alpha_s = \frac{C_{H_2O}/C_{EtOH}}{X_{H_2O}/X_{EtOH}} \quad (7)$$

Where X and C are the volume fractions of species in the feed and sorbed-membrane, respectively.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Monomer Concentration

Figure 2 reveals the effect of monomer concentration on %conversion and %GE. Evidently, the polymerization of HEMA almost completed because persulfate radicals mostly reside in the aqueous phase where they can easily react with water-soluble HEMA monomer. Grafting of PHEMA on NR increased with HEMA concentration. This is because increasing HEMA monomer concentration provides higher probability of monomer or active oligomers to react with active grafting sites on NR surfaces [7].

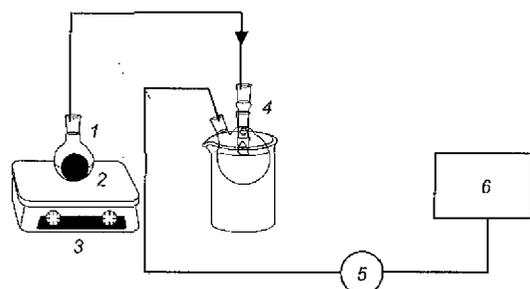


Figure 1 Schematic diagram of desorption apparatus: (1) Sample container (2) Swollen membrane (3) Heater (4) Cold trap with liquid nitrogen (5) Pressure gage (6) Vacuum pump

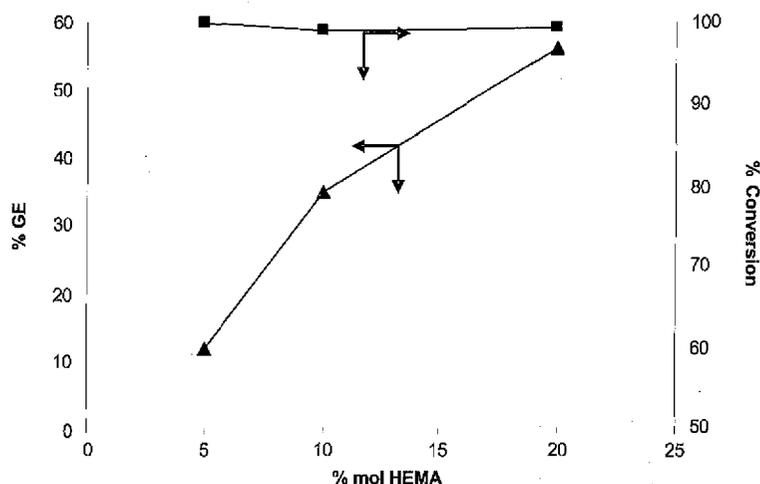


Figure 2 Effect of the monomer concentration on grafting of PHEMA on NR latex particles; initiator concentration is 0.5%mol (base on monomer)

3.2 Effect of Initiator Concentration

The effect of the initiator concentration on %GE and %conversion was illustrated in Figure 3. Expectedly, increasing initiator concentration generated more active radicals resulting in the increasing of the HEMA conversion. Nevertheless, %GE showed an increase at low concentration of the initiator, then %GE reached the maximum and

decreased for high initiator concentration. This is because the active sites on NR particles were fully occupied by PHEMA growing-chains and thus more generated-radicals will produce more homo-PHEMA instead of grafted ones [8].

3.2.1 FT-IR

Figure 4 shows FT-IR spectra of NR, NR-g-PHEMA and PHEMA. The characteristic peaks of NR was

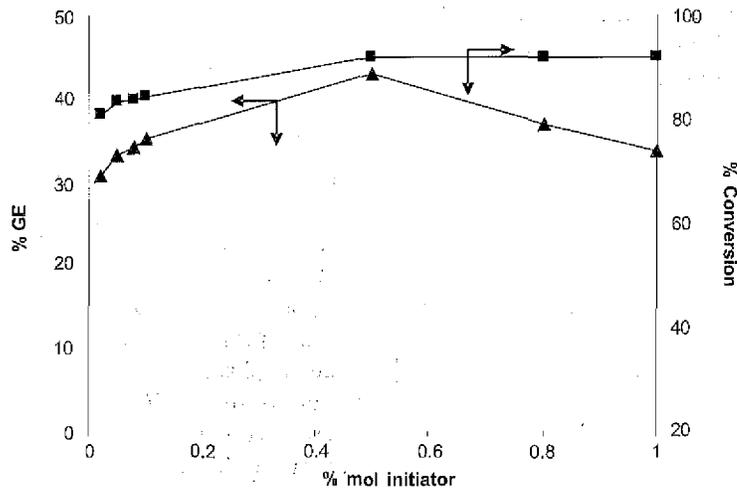


Figure 3 Effect of the initiator concentration on grafting of PHEMA on NR latex particles; monomer concentration is 5%mol (base on NR)

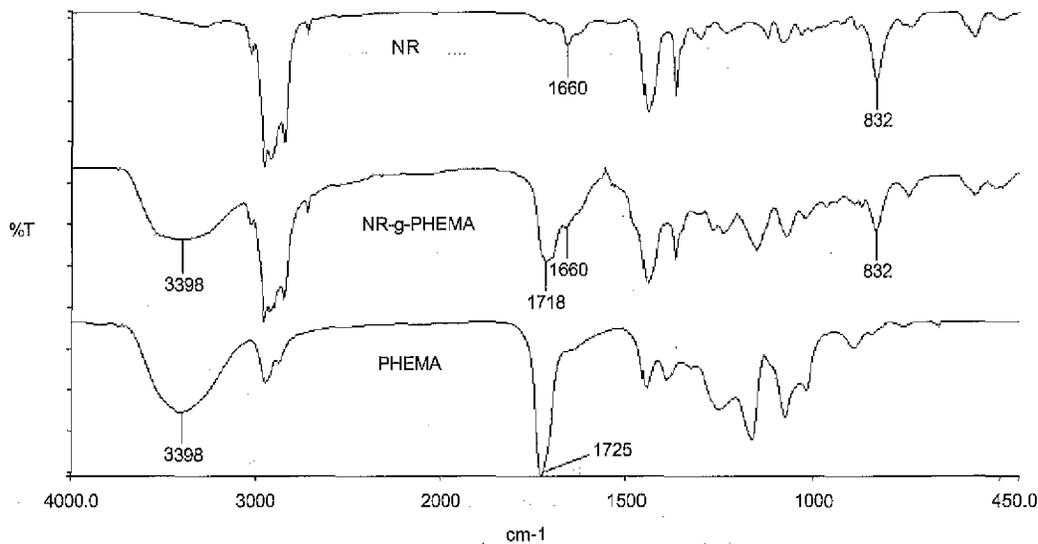


Figure 4 FT-IR spectra of NR, NR-g-PHEMA and PHEMA

observed at 1660 cm^{-1} and 832 cm^{-1} attributing to C=C stretching and bending of the isoprene unit. The C=O and OH of PHEMA can be observed at 1736 cm^{-1} and 3409 cm^{-1} respectively. For NR-g-PHEMA, the characteristic peaks of both NR and PHEMA were evident which indicates the successful grafting of PHEMA on NR latex particles.

3.2.2 States of Water

As shown in Figure 5, DSC thermograms of the NR-g-PHEMA membranes revealed only endothermic peaks at 0°C suggesting that the water molecules were clustered in the form of free water. Figure 7 shows the content of water corresponding to free water, non-freezing bound and total water as a function of %GE. The free

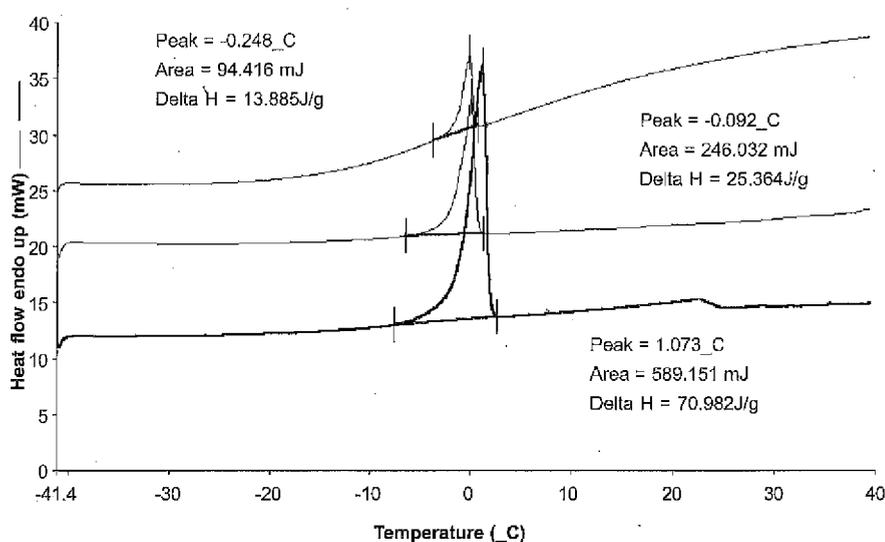


Figure 5 DSC thermograms of absorbed-water in the NR-g-PHEMA membranes

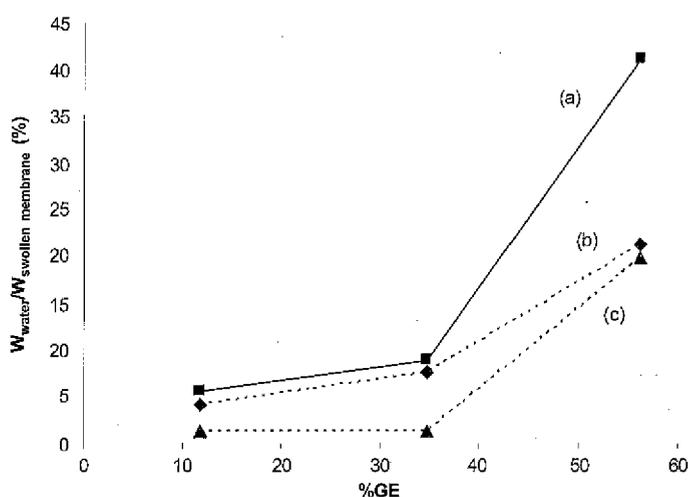


Figure 6 Water content in the NR-g-PHEMA membranes corresponding to (a) total water (b) free water and (c) non-freezing bound water

water and non-freezing bound water increased with increasing %GE because as increasing grafted-PHEMA more hydroxyl groups are available to interact with water molecules.

3.2.3 Swelling Behavior

Figure 7 shows the swelling degree of NR-g-PHEMA membranes as a function of acetone concentration. The swelling degree increased with increasing %GE and showed a maximum at about 70 %v/v acetone composition. This non-ideal behavior occurred due to the coupling between water and acetone molecules [5].

Table 1 shows the interaction parameter of acetone and water with NR-g-PHEMA membranes as calculated by equation (6). It was found that the interaction parameters for water is slightly lower

Table 1 Interaction parameters of water and acetone in NR-g-PHEMA membranes

%GE	χ_{ip}	
	Water	Acetone
11.77	1.15	1.30
34.83	1.22	1.66
56.15	0.90	1.09

than those of acetone indicating the preferential sorption of water in the membranes.

3.2.4 Mechanical Property

As revealed in Table 2, the initial modulus and tensile strength at break increased with increasing

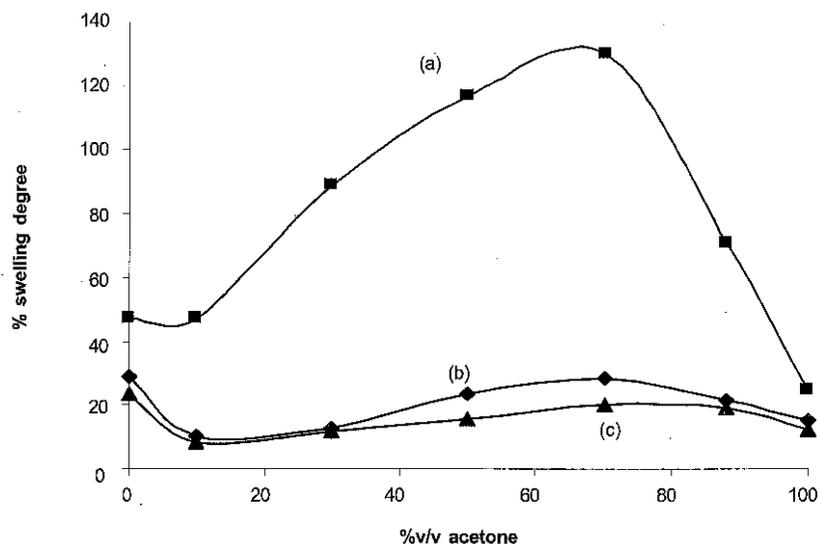


Figure 7 Swelling degree of NR-g-PHEMA at %GE (a) 56.15% (b) 34.83% and (c) 11.77%

Table 2 Mechanical property of NR-g-PHEMA membranes

%GE	Initial modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)	Modulus at 100% (MPa)
11.77	0.08	0.06	763.74	0.05
34.83	0.13	0.20	630.02	0.08
56.15	5.43	2.10	394.47	1.29
NR	0.26	3.52	1231.71	0.29

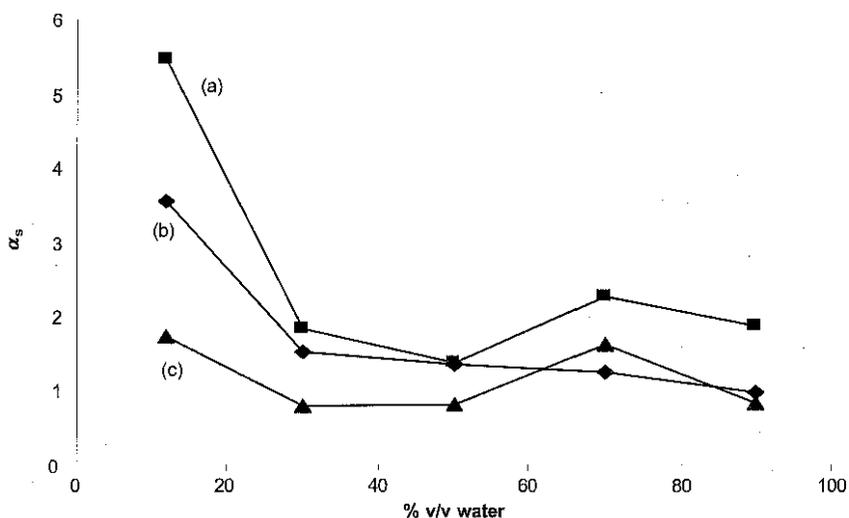


Figure 8 Water sorption selectivities of NR-g-PHEMA membranes as a function of water content in water-acetone mixtures; (a) %GE = 56.15 (b) %GE = 34.83 and (c) %GE = 11.77

%GE but the elongation at break decreased. This is because the PHEMA is semi-crystalline polymer which is more brittle than NR.

3.2.5 Sorption Study

Figure 8 shows the water sorption selectivity (α_s) of NR-g-PHEMA membranes. The sorption selectivity decreased with increasing water concentration in water-acetone mixtures and increasing PHEMA content in the membranes. Because the membrane with high PHEMA content is highly swelled in water, increasing water concentration causes the free volume of the membrane to increase allowing more acetone molecules to access the membrane structure.

4.0 CONCLUSIONS

The NR latex particles grafted with PHEMA was prepared by emulsion polymerization technique. The grafting efficiency increased with increasing monomer and initiator concentrations. The FT-IR study confirmed the successful grafting of PHEMA on NR. The modulus of the membranes increased and the elongation at break decreased with increasing %GE. The swelling degree of the

membranes in water-acetone mixtures showed a maximum swelling at 70%v/v of acetone. However, the calculated interaction parameters suggested the sorption preference of the membranes to water. Studied by DSC, the bound water was found to increase with increasing %GE due to the increasing number of hydroxyl groups of PHEMA. The sorption selectivities of the membranes increased with increasing grafted-PHEMA but, as the water content in the water-acetone mixtures increased, the sorption selectivity declined.

REFERENCES

- [1] Hsueh, C.L., J.F. Kuo, Y.H. Huang, C.C. Wang, and C.Y. Chen. 2005. Separation of Ethanol-water Solution by Poly(acrylonitrile-co-acrylic acid) Membranes. *Sep. Pur. Tech. J.* 41: 39-47.
- [2] Buyanov, A.L., L.G. Revel'skaya, Yu. P. Kuznetsov, and A.S. Shestakova. 1998. Cellulose-poly(acrylamide or acrylic acid) Interpenetrating Polymer Network Membranes for the Pervaporation of Water-ethanol Mixture. *J. Appl. Polym. Sci.* 69: 761-769.

- [3] Ruckentein, E., and L. Liang. 1996. Poly(acrylic acid)-Poly(vinyl alcohol) Semi- and Interpenetrating Polymer Network Pervaporation Membranes. *J. Appl. Polym. Sci.* 62: 973-987.
- [4] Chiang, W.Y., and C.L. Chen. 1998. Separation of Water-alcohol Mixture by using Polymer Membranes-6. Water-alcohol Pervaporation through Terpolymer of PVA Grafted with Hydrazine Reacted SMA. *Polym. J.* 39: 2227-2233.
- [5] Ping, Z.H., Q.T. Nguyen, S.M. Chen, J.Q. Zhou, and Y.D. Ding. 2001. States of Water in Different Hydrophilic Polymer-DSC and FTIR studies. *Polym. J.* 42: 8461-8467.
- [6] Mandal, S., and V.G. Pangarkar. 2002. Separation of Methanol-benzene and Methanol-toluene Mixtures by Pervaporation: Effects of Thermodynamics and Structural Phenomenon. *J. Membr. Sci.* 201: 175-190.
- [7] Kawahara, S., T. Kawasura, T. Sawada, and Y. Isono. 2003. Preparation and Characterization of Natural Rubber Dispersed in Nano-matrix. *Polymer* 44: 4527-4531.
- [8] Joshi, J.M., and V.K. Sinha. 2006. Graft Copolymerization of 2-hydroxyethyl-methacrylate onto Carboxymethyl Chitosan using CAN as an Initiator. *Polym. J.* 47: 2198-2204.
- [9] Ray, S., and S.K. Ray. 2006. Effect of Copolymer Type and Composition on Separation Characteristics of Pervaporation Membranes-A Case Study with Separation of Acetone-water Mixture. *J. Membr. Sci.* 270: 73-87.