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Preparation of Poly Methyl Acrylate Membrane by Template Polymerization Method

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Poly methyl acrylate membrane in bulk has been synthesized in the presence of poly methyl methacrylate (template) at 65 ± 0.1 ºC for 1.5 h using benzoyl peroxide as an initiator. The present work focuses the synthesis of hydrophobic polymeric membrane through template polymerization, in order to confirm the nature of polymeric membrane.

Key Words: Poly methyl acrylate, Template polymerization, Solubility, Chemical resistance.

INTRODUCTION

Membrane is a thin porous sheet which when placed between two phases may allow selective mass to transport. The synthesis of membrane has revolutionized the research area due to their industrial significance[1]. The survey of literature shows very few reports regarding the synthesis of polymeric membrane through template polymerization. The applicability of polymers, whether elastomers, plastics or fibres to end uses such as fabrics, membrane[2-4], film coating or foams can be broaden in scope by using chemical reaction to crosslink template with different monomers to modify their structure and thus properties of daughter polymers produced during template polymerization[5,6].

EXPERIMENTAL

Analytical grade reagents methyl methacrylate (Robert Johnson) and methyl acrylate (Ranbaxy) contains impurities of hydroquinone which was removed by repeated washing with 4 % NaOH solution and water[7,8]. The purified methyl acrylate and methyl methacrylate were dried over anhydrous sodium sulphide and silica gel, respectively. The monomers were subjected to vaccuum distillation and stored in refrigerator for experimental work.

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2,2′-Azodiisobutyronitrile (AIBN) (E. Merck) was recrystallized thrice from methanol. Benzoyl peroxide was purified by dissolving it in chloroform at room temperature and adding twice the volume of methyl chloride. The compound melts at 106 ºC with decomposition[9]. The solvents were used as such without further purification.

Preparation of poly methyl methacrylate template: Poly methyl methacrylate was obtained by polymerizing methyl methacrylate (5.32 mol L^{-1}) in dry benzene under nitrogen at 65 ºC using AIBN (0.01 mol L^{-1}) as initiator.

Casting of poly methylacrylate membrane: The concentrate emulsion of poly methylacrylate was prepared by dissolving poly methyl methacrylate in methylacrylate. This solution is stirred for 1 h there after, benzoyl peroxide was added. This whole content was again subjected to stirring for 1 h.

The sample solution of methylacrylate, poly methyl methacrylate and benzoyl peroxide content in a glass ampoule was flushed with nitrogen for 3 min. The filled glass ampoule was then placed in a thermostat bath for 1.5 h at 65 ± 0.1 ºC.

The glass plates (12" × 5" × 3/16") used for membrane casting, were treated with a mixture of conc. H_2SO_4 and $K_2Cr_2O_7$ and washed and dried in oven at 60 ºC for 1 h. The membrane was then casted by pouring the concentrated solution on the clean dry glass plates and tilting it to and fro to spread the solution on the glass plate uniformly. The membranes were kept at the room temperature for 2 d for drying purpose. The amount of components involve in the preparation of poly methyl acrylate membrane are listed in Table-1.

TABLE-1
COMPONENTS INVOLVED IN THE PREPARATION OF PMA MEMBRANE

Membrane code	PMMA (mol L^{-1})	MA (mol L^{-1})	BPO (mol L^{-1})	Toluene (mL)	Temp. (ºC)	Time (min)
1	6.00	11.0	6.88	-	65	90
2	5.00	11.0	6.88	-	65	90
3	3.60	11.0	6.88	-	65	90
4	6.00	11.0	6.88	0.5	65	90
5	6.00	11.0	6.88	1.0	65	90

PMMA = Poly methyl methacrylate; MA = Methyl acrylate;
BPO = Benzoyl peroxide

Characterization of poly methyl methacrylate template: The NMR spectra was recorded on a varian 100 HA spectrometer using acetone (d_6) and $CDCl_3$ as solvents, respectively and tetra methyl silane as internal reference. The multiplet peak which appears in the region 6.0-6.3 τ is assigned for methoxy proton. The methylene protons appears at 8.25 τ as singlet. The methine protons are marked by triplet peak at 8.70, 8.85, 9.00 τ.

RESULTS AND DISCUSSION

Absorption experiment: To understand the kinetics of absorption, membrane strips (*ca.* 50 mg by weight) were immersed in various chemicals at varying temperature. After various relatively short time, the increase in weight due to absorption was determined with the help of a electronic balance.

The first stage in polymer dissolution is characterized by a slow penetration of the solvent molecules into the interstices of polymer coil and forcing them to swell. During the swelling stage the volume of polymer matrix increases and the solvent molecules leave the solvent phase and diffuse into the polymer matrix. The phenomenon of swelling depends purely on the force of interaction between solvent molecule and polymer segments. Water, ethylene glycol, cyclohexane are used as test liquids. The absorption of cyclohexane in PMA membrane is highest while ethylene glycol also exhibits high absorption but the absorption of water is relatively low (Fig. 1). The low absorption of water and ethylene glycol compared with that of cyclohexane is in agreement with the low solubility parameters.

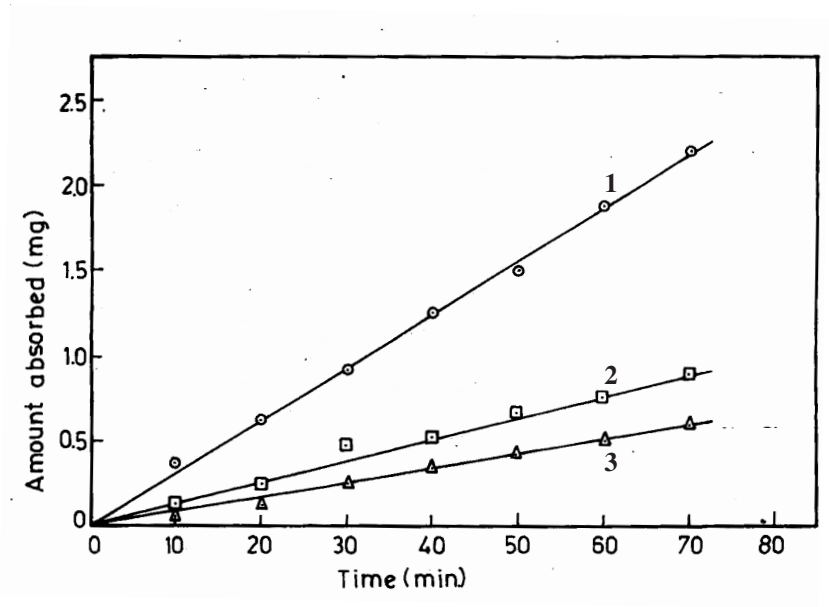

Fig. 1. Amount absorbed of polymethyl acrylate membrane from solvents as a function of time at 35 ºC (1, 2, 3) absorption of cyclohexane, ethylene glycol and water

The equilibrium absorption of water and ethylene glycol, obtained from the solubility experiment are 0.6 and 0.9, respectively at 35 ºC in polymeric membrane.

Concerning the behaviour of binary mixture of water-ethylene glycol, the absorption is larger for higher (ethylene glycol) and decreases with decreasing the (poly methyl methacrylate), (template) in the membrane (Fig. 2). In order to investigate the effect of temperature on the absorption, the investigations are made at 35 and 65 ºC, respectively, in presence of water-ethylene glycol mixture (Fig. 3). The data show that the amount absorbed increases with temperature. The absorption remains unaffected with the variation of molecular weight of template employed for the composition in the membrane.

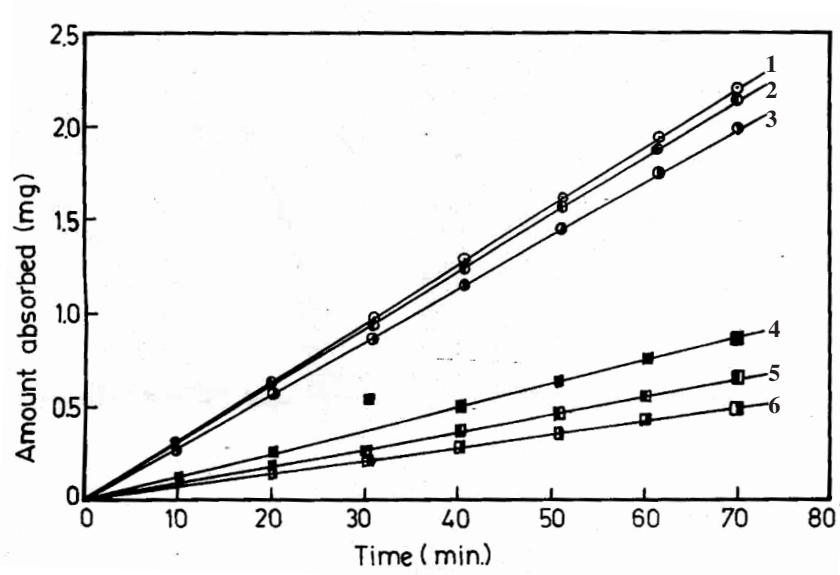

Fig. 2. Weight absorbed of polymethyl acrylate membrane from ethylene glycol-water mixture as a function of time at 65 ºC (1, 2, 3) absorption from cyclohexane PM1, PM2 and PM3 and (4, 5, 6) water/ethylene glycol mixture in polymethylacrylate membrane PM1, PM2, PM3

Solubility and chemical resistance: The membrane strips (*ca.* 50 mg by weight) were immersed in various organic and inorganic solvents like conc. H_2SO_4, HCl, HNO_3, DMF, DMSO, dioxane, benzene, methanol. *etc.* for 7 d. The variation in the weight was determined with the help of electronic balance.

Table-2 reveals that poly methylacrylate membrane gets swell in presence of strong acids *viz.*, conc. H_2SO_4, conc. HCl, conc. HNO_3. It is possible because of the solvent-solute interaction and unfolding of the segments constitute a slow process. While the membrane soluble in most of the organic solvents *viz.*, DMF, DMSO, dioxane, ethyl acetate benzene, acetonitrile, dichloromethane and chloroform. The solubility of the membrane in methanol, diethyl ether and hexane is 0.126, 0.09 and 0.075 %, respectively.

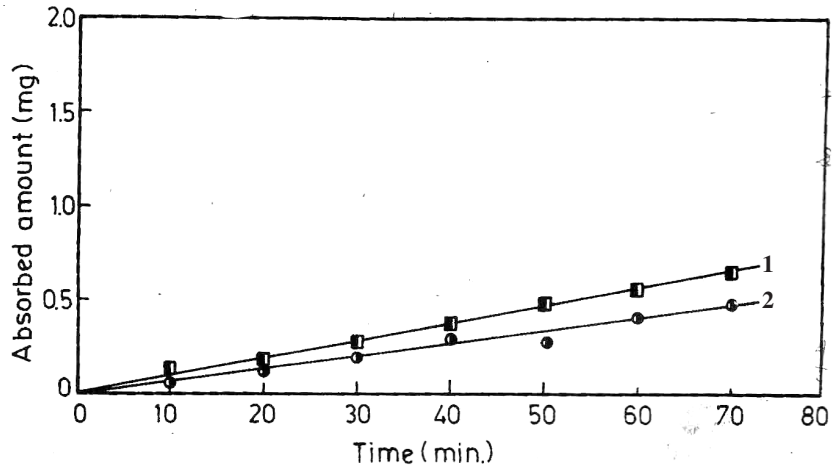

Fig. 3. Amount absorbed of polymethyl acrylate membrane PM2 from water-ethylene glycol mixture as a function of time at different temperature (1 , 2) at 60 ºC and 40 ºC

TABLE-2
SOLUBILITY OF POLYMETHYL ACRYLATE MEMBRANE

Solvent used	Membrane 1	Membrane 2	Membrane 3
Chloroform	++	++	++
Hexane	+	+	+
Diethyl ether	+	+	+
Methanol	+	+	+
Acetonitrile	- +	+	+
Benzene	- +	+	+
Dioxane	++	++	++
DMF	++	++	++
Ethylacetate	++	++	++
Nitric acid	- -	- -	- -
HCl	- -	- -	- -
Sulfuric acid	- -	- -	- -

++ soluble at once; - + soluble after 24 h; - - resistant; + sparingly soluble.

Conclusion

On the basis of experimental data interpretated, it is concluded that in the present system, poly methyl acrylate membrane shows high absorption with cyclohexane where as lowest with water and also shows acid resistant character. Such membranes have practical applicability in industrial purposes.

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