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THE EFFECT OF CROSSLINKING TEMPERATURE UPON DENSITY AND SWELLING DEGREE OF PDMS, PEG, PES AND PAN MEMBRANES

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ABSTRCT

In this research for fabricated the membranes usagea blend of polymers that are comprised of PDMS (poly dimethylsiloxane), PEG (poly ethylene glycol), PES (poly ether sulfonic) and PAN (poly acryl nitrile) as polymers, a symmetric poly ester ultra-filtration membranes, PES, PVP (poly vinyl pyrrolidone) and N,N-Dimethyl acetamide (DMAc) as solvent used for fabricated of support layer with cross linking TEOS (tetra ethyl ortho silicate) as silica Nanoparticles (cross linking agent), ammonia as catalyst/inducer and span 80 as surfactant. In the research, four kinds of membrane including PDMS, blend of PDMS and PEG, blend of PDMS and PES, and blend of PDMS and PAN are used. In this research, variation of crosslinking temperature (T), from 65-85 Ċ upon density of membranes (ρ_p), swelling degree (M_{sD}) and %swelling by volume, is studied. It was observed that with increase the crosslinking temperature, ρ_p is increased and M_{sD} ,%swelling by volume is decreased.

KEYWORDS: PDMS, TEOS, crosslinking Temperature, crosslinking agent, swelling degree

INTRODUCTION

Currently, one area of intense research focus is on processes that can be implemented for different gas species using membrane technologies, due to the unique advantages that these technologies possess. Such advantages include stability, passive operation, low cost and mechanical robustness [1]. However, these membranes can only be viable in many procedures such as separation, filtration, purification as well as isolation of liquid and gas phases (gas permeable barrier), if they possess both high permeability and selectivity. The cost of many of these procedures is directly proportional to the flux of the membranes, which is related to the permeability. Polydimethylsiloxane (PDMS) is a commonly used material for many permeable gas membrane applications as it is known for showing a high permeability to a wide range of gas species, while being biocompatible, cheap and easy to use[2]. PDMS has already been employed for gas separation or, in its intrinsic form, as a gas permeable barrier. It has also been employed in mixed matrix and co-polymer membranes for gas separation, purification and effective permeable barriers [3]. Within a non-porous rubbery polymer, such as PDMS, gas permeation is usually described by the solution–diffusion mechanism [4]. This mechanism involves three steps: (1) absorption at the upstream boundary, (2) diffusion through the membrane and (3) desorption on the downstream boundary. The ability to control the absorption, diffusion and desorption of the gas molecules, by engineering the structure of the polymer, can be a desirable property. Whether to increase the permeation rate through the membrane for gas sensing applications or to enhance the selectivity for industrial processes, the control of the free volume to optimize flux is a critical challenge to overcome. Environmental concerns have resulted in legislations that place strict limits on the sulphur content of vehicle fuel. For instance, in the European Union, a maximum sulphur level of 50 ppm has been stipulated by 2005, with a further reduction to a maximum of 10 ppm nowadays [5–6]. Currently, hydro desulfurization (HDS) serves as the most commonly used and efficient technique for sulphur removal [7]. In recent years, membrane process has attracted increasing attention due to its potential advantages overconventional desulfurization processes, including greater selectivity towards thiophene over olefins, lower operation and energy costs, without hydrogen source and co product of H2S gas. Poly dimethyl siloxane (PDMS) has been demonstrated as one of the most widely utilized membrane materials for pervaporative desulfurization [8], owing to its outstanding aging resistance, thermal/chemical stability, good process ability, in particular its superior permeability to small molecules [9]. Moreover, according to solubility parameter theory, the solubility parameter (δ) of PDMS (δ= ~ 21.0) is close to the solubility parameter of thiophene and its derivatives (δ varied from ~ 19.0 to ~ 20.0) [10]. İn our previous work [11-14],the effect of crosslinking temperature upon PDMS and blending of PDMS with PEG,PES and PAN polymers were studied so effect of TEOS as crosslinking agent upon PDMS and blending of PDMS with PEG,PES and PAN were investigated.[15-18] In recent years, elastomeric polymer–inorganic Nano composites have been the subject of a huge scientific interest. Theoretically, by introducing inorganic fillers into elastomers, the Nano composites will exhibit dramatically improved bulk properties. The accompanying local stress and interface defects may substantially worsen the mechanical properties of the Nano composite membranes. On the other hand, since PDMS is usually dissolved in non aqueous oil-based solvent, it is quite difficult and even impossible to manipulate the simultaneous hydrolysis–condensation of silicon precursors and cross-linking of PDMS oligomers in a homogenous phase. However, this process was severely restricted by the diffusion of silicon precursor and water within PDMS network. Moreover, the process is difficult to control and the consumption amount of chemical reagents including eco-unfriendly organic solvent is quite large. In the current study, different kinds of membrane materials, fabricated from small silica-precipitating inducer/catalyst and various silica precursors, were extensively investigated. As a proof-of-principle, PDMS-SiO_2 Nano composite membranes were in-situ fabricated through the synergy of polymerization of PDMS oligomers in the oil phase with silica precipitation in the reverse micro emulsion. NH_3 was used as inducer/catalyst. Tetraethyl ortho silicate (TEOS) was used as the silica precursors. The hydrolysis and condensation occurred when the inorganic precursor and the inducer molecules encountered at the water–oil interface. The size and nanostructures of silica could be readily tuned through a rational synergy among hydrolysis/condensation rates, silica- precipitating inducer type, geometry, interfacial constraints and the size of water droplets in PDMS matrix.

Experimental

Membrane material

Tetraethyl orthosilicate (the corresponding average molecular weight was around 208),poly dimethyl siloxane oligomer(the viscosity was 5000 mpa.sec and the corresponding average molecular weight was around 40000),poly ethylene glycol(the corresponding average molecular weight was around 4000),poly ether sulfone (the corresponding average molecular weight was around 58000),poly acryl nitrile(the corresponding average molecular weight was around 45000), poly vinyl pyrrolidone(the corresponding average molecular weight was around 360000), N,N-Dimethyl acetamide as solvent for fabricated of support layer with specific gravity of 0.937, a symmetric poly ester ultra-filtration membranes used as support, n-heptane as solvent with specific gravity of 0.6835 and De-ionized water from a Millipore ultrapure water system was used in all the experiments.for estimation density of membranes usage of ethanol with specific gravity of 0.78 as the auxiliary liquid.

Synthesis blending of the PDMS,PEG,PES and PAN with SiO_2 Nano composite membranes

Certain amount of Span 80 as surfactant, silicon precursor, as well as PDMS and PEG oligomer were dissolved in n-heptane at room temperature to make a homogeneous solution. Inducer aqueous solutions were suspended with a concentration of 0.5 molar (ammonia was dissolved in a 25 milli molar Tris-HCl buffer solution at neutral PH). And then specific amount of the above aqueous solution was drop wise added into the oil solution under vigorous mechanical stirring. After stirring for 30 minute, small amount of dibutyltin dilaurate was added. After degassing, the solution was cast onto the support layer,the solution for the support layer was prepared by dissolving 15wt% PES and 3wt% of PVP in N,N-Dimethyl acetamide.the homogeneous solution,cast on a a symmetric poly ester ultra-filtration membranes,was immersed immediately in a distilled water for remove the remaining DMAc.The membranes were first dried in air for 24 hours and then thermally annealed at 65- 85ċ to accomplish Cross-linking and evaporate the residual solvent. After that, the membranes were washed by De-ionized water and dried at room temperature. All samples were stored in dust free and dry environment before the pervaporation measurements. Now for fabricated blending of polymers PDMS and PES,PDMS and PAN repeated too,only enough which PEG omitted from medium and replace with PES and PAN.

Basic principle

Swelling measurements are often used to measure the crosslink density of TEOS.the degree of swelling (the amount of solvent imbibed) is known to be dependent upon the crosslink density of polymer (PDMS , blending of PDMS and PEG,blending of PDMS and PES and blending of PDMS and PAN) network; the greater the crosslink density, the less the degree of swelling. Percentage swelling by volume of the polymer samples can be determined by using the following formula [19]:

$$\text{\% swelling by volume} = \frac{\text{Gain in weight}}{\text{specific gravity of solvent}} * \frac{\text{specific gravity of specimen}}{\text{original weight of specimen}} (1)$$

Density measurements were determined using the hydrostatic weighing method utilizing a Mettler Toledo balance (Model XS205, Switzerland) and density determination kit [20, 21]. The membrane density (ρ_p) was calculated by:

$$\rho_p = \frac{M_A}{M_A - M_L} \rho_0 (2)$$

Where M_A is the membrane weight in air, M_L is the membrane weight in the auxiliary liquid and ρ_0 is the density of the auxiliary liquid. For the determination of density of PDMS, blending of PDMS and PEG,blending of PDMS and PES and blending of PDMS and PAN membranes, ethanol was used as the auxiliary liquid. Solvent swelling measurements were carried out by using pre weighed dry membranes of the different weight of crosslinking agent (M_{dry}), immersing them in pure heptanes until equilibrium swelling to be reached. The membranes were then pat dried and immediately weighted (M_{wet}).the swelling degree (M_{SD}) of the membranes was then calculated by:

$$M_{SD} = \frac{M_{wet} - M_{dry}}{M_{dry}} * 100 \quad (3)$$

RESULTS AND DİSCUSSİON

In this research, variation of cross linking temperature (T), from 65-85 Ċ upon density of membranes (ρ_p), swelling degree (M_{sD}) and %swelling by volume, is studied. In this research usage of blend of polymers that are comprised of PDMS (poly dimethylsiloxane), PEG (poly ethylene glycol), PES (poly ether sulfonic) and PAN (poly acryl nitrile) as polymers, a symmetric poly ester ultra-filtration membranes used as support with cross linking TEOS (tetra ethyl ortho silicate) as silica Nano particles (cross linking agent), ammonia as catalyst/inducer and span 80 as surfactant.

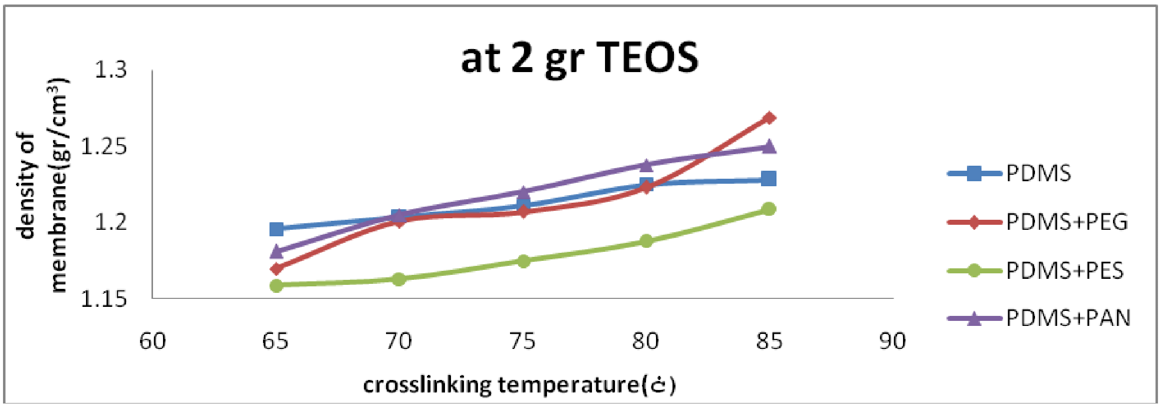

Figure.1. ***variation of density of membrane with crosslinking temperature***

Fig.1 shows the changes of density of membrane by crosslinking temperature for a situation in which 2 grams of TEOS is used to make respective membranes as a crosslinking agent.According to this figure,with increased the crosslinking temperature, density of membranes is increased. highest effect of membrane crosslinking temperature on the density of membrane is for case of blending of PDMS and PEG polymers is used to make the membranes, and reason this is which usage of blending technic's of polymers cause improved properties of membranes.This is to be expected as the increasing crosslinking temperature causes the polymerization to form a tighter network and therefore increasing the density.

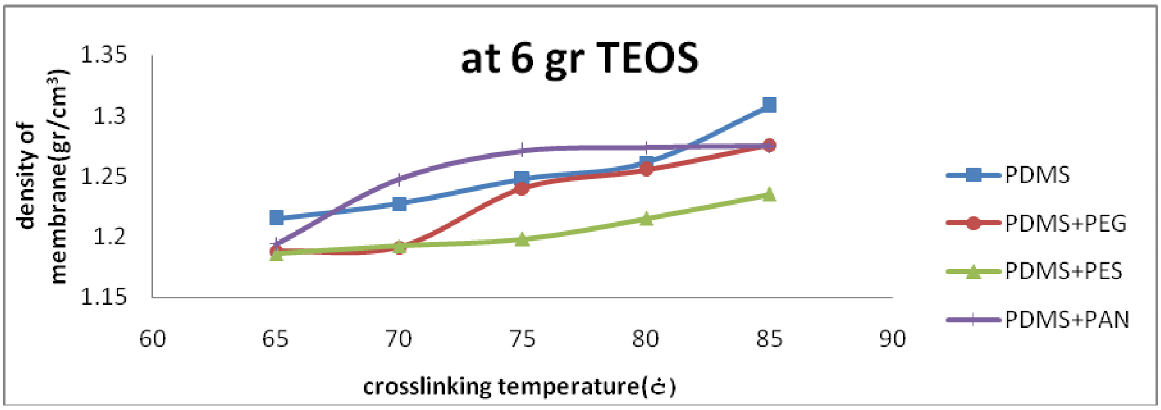

Figure.2. ***variation of density of membrane with crosslinking temperature***

Fig.2 shows the changes of density of membrane by crosslinking temperature for a situation in which 6 grams of TEOS is used to make respective membranes as a crosslinking agent.According to this figure, with increased the crosslinking temperature, density of membranes is increased.Changes in fig.2 are relatively similar to fig.1, except that in this situation, changes occur more severely

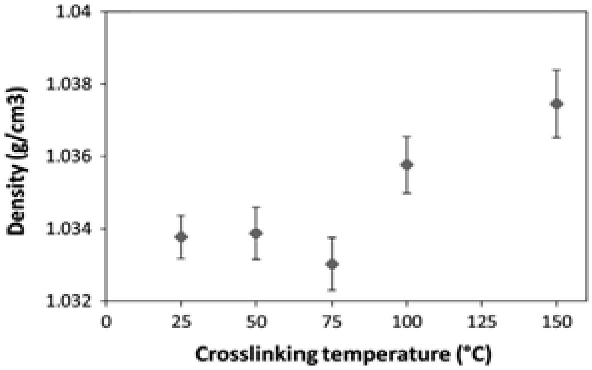

Figure.3. *variation of density of membrane with crosslinking temperature [22]*

It can be seen with fig. 3, as an overall trend is that when the crosslinking temperature is increased the density of the membrane increases as well. This is to be expected as the increasing crosslinking temperature causes the polymerization to form a tighter network and therefore increasing the density. However, the membrane crosslinked at 75 °C shows a decrease in density compared to the membrane cross linked at 50ċ.according to fig. 3,with increasing the temperature crosslinking from 65-85ċ,density of membranes is increased.

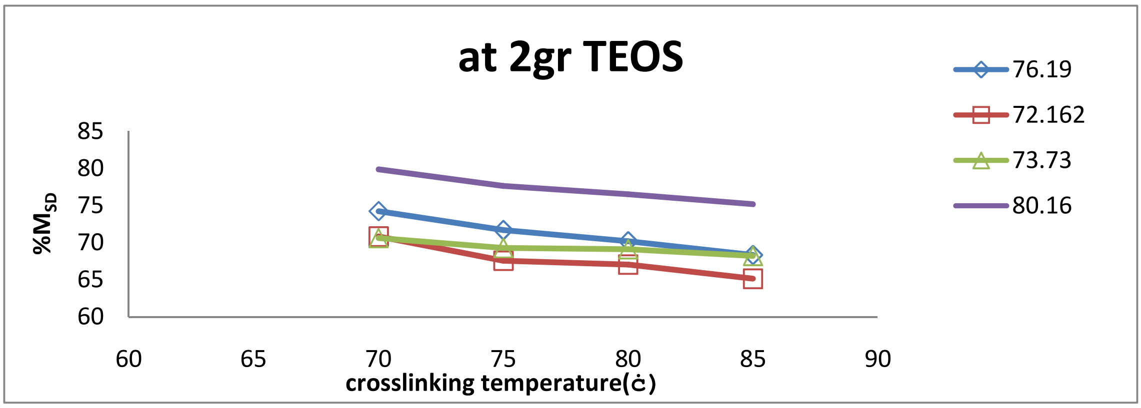

Figure.4. *variation of percent swelling degree with crosslinking temperature*

Fig.4 shows the changes of swelling degree of the membranes by crosslinking temperature for a situation in which 2 gram TEOS are used to make respective membranes as a crosslinking agent.Based on these figures, by increasing crosslinking temperature, %swelling degree of membranes is decreases. Such observations have been ascribed to a reduced chain length of the oligomers between crosslinks [23], this shortening of the chains between crosslinks enhances the elastic resistance to the swelling stress and therefore lowers the degree of swelling [24, 25]

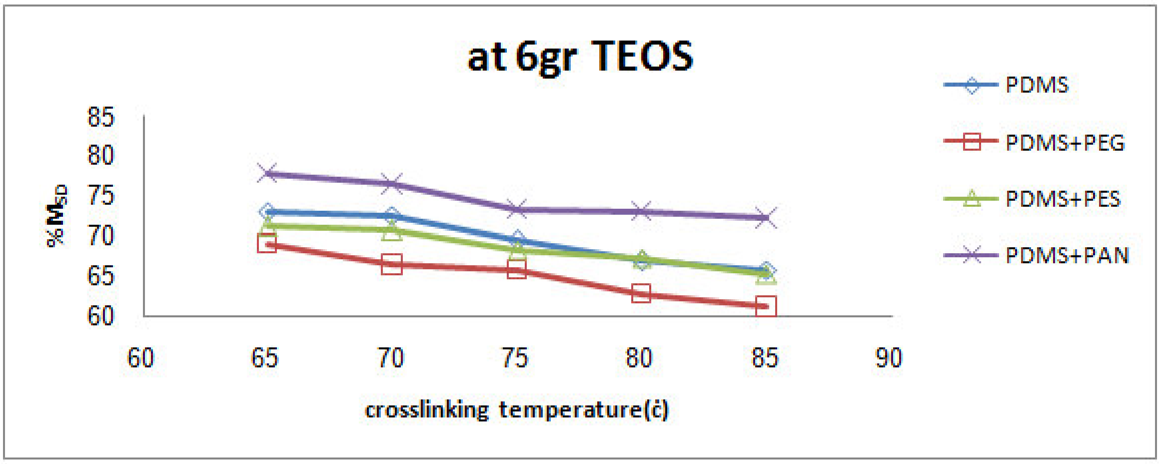

Figure.5. *variation of percent swelling degree with crosslinking temperature*

Fig.5 shows the changes of swelling degree of the membranes by crosslinking temperature for a situation in which 6 gram TEOS are used to make respective membranes as a crosslinking agent.Based on these figures, by increasing crosslinking temperature, %swelling degree of membranes is decreases.Changes in fig.5 are relatively similar to fig.4, except that in this situation, changes occur more severely.

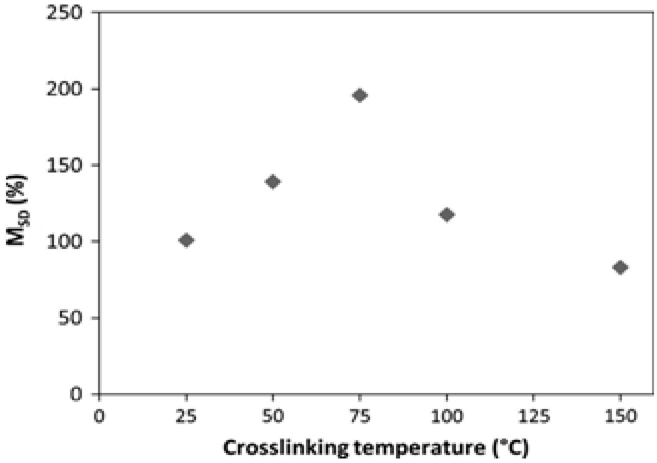

Figure.6. *variation of swelling degree with crosslinking temperature [22]*

Fig.6 shows the changes of swelling degree of membranes by cross linking temperature in toluene. According fig.6, in general state, with increasing the temperature crosslinking, swelling degree of the membranes decreases.According to fig. 6, with increasing the temperature crosslinking from 65-85ċ, swelling degree of membranes is decreased.

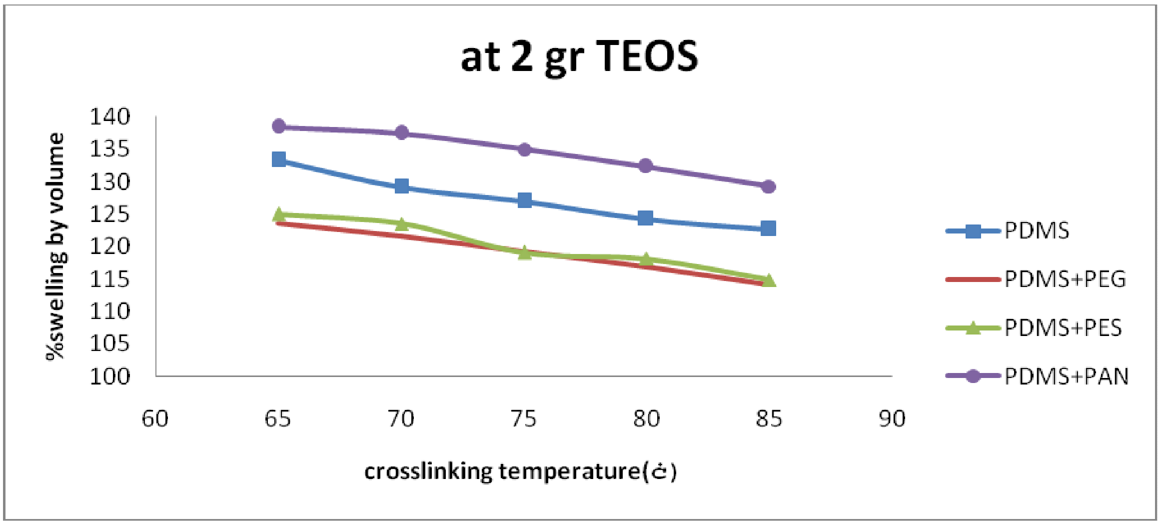

Figure.7. *variation of percent swelling degree by volume with crosslinking temperature*

Fig.7 shows the changes of %swelling by volume of the membranes by crosslinking temperature for a situation in which 2 gram TEOS are used to make respective membranes as a crosslinking agent.Based on these figures, by increasing crosslinking temperature, %swelling by volume of membranes is decreases.

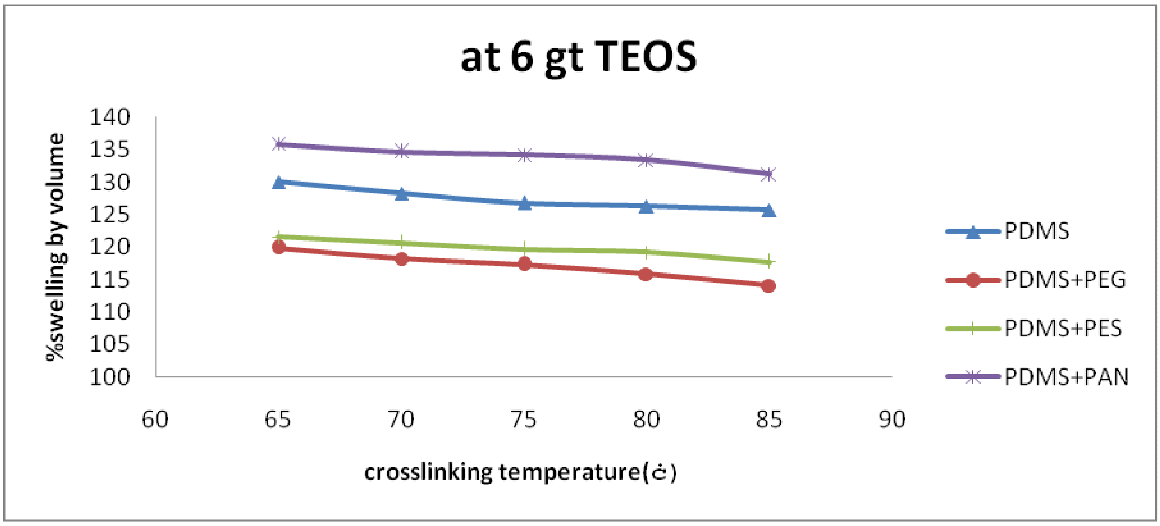

Figure.8. ***variation of percent swelling degree by volume with crosslinking temperature***

Fig.8 shows the changes of %swelling by volume of the membranes by crosslinking temperature for a situation in which 6 gram TEOS are used to make respective membranes as a crosslinking agent.Based on these figures, by increasing crosslinking temperature, %swelling by volume of membranes is decreases.

CONCLUSIONS

Crosslinking the polymer in the membrane technology makes it insoluble in the feed mixture and decreases its swelling in order to derive a good selectivity. The effect of crosslinking temperature of membranes upon density of membranes (ρ_p), swelling degree (M_{sD}) and %swelling by volume, is studied. It was observed that with increase the crosslinking temperature, ρp is increased and M_{sD} ,%swelling by volume is decreased. According fig.4, 5, 7and8, because blending of PDMS and PEG has minimum swelling degree and % swelling by volume, it means, this blending have good selectivity for special spice, so according fig.5 and fig.8 versus fig.4 and fig .7, with increasing the weight of crosslinking agent (6 grams versus 2 grams), swelling degree and % swelling by volume for all of blending of polymers in this research is decreased.

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