

Structure and performance of PDMS as cross-linking agent upon property of blending PDMS, PEG, PES and PAN membranes

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In this research for fabricated the composite membranes usage a blend of polymers that are comprised of PDMS (polydimethylsiloxane), PEG (polyethylene glycol), PES (polyether sulfonic) and PAN (poly acryl nitrile) as polymers, asymmetric polyester ultra-filtration membranes, PES, PVP (polyvinyl pyrrolidone) as pore former and N,N-Dimethyl acetamide (DMAc) as solvent used for fabricated of support layer with crosslinking PDMS as crosslinking agent, ammonia as inducer, dibutyltin dilaurate as catalyst and span 80 as surfactant. In the research, four kinds of the membrane including PDMS, blend of PDMS with PEG, blend of PDMS with PES and blend of PDMS with PAN are used. The structural morphology of support and active layers of the composite membranes was characterized with SEM. In this research, crosslinking temperature and crosslinking time are fixed and 70°C and 1 hour respectively so this study focuses on the variation of crosslinking agent (PDMS) (1.5, 3, 4.4, 5.8 and 7.15 wt%) upon crosslinking density (V_e), swelling degree (M_{SD}), %swelling by volume, density of membrane specimen (ρ_p), volume fraction of rubber phase (V_2) and number average molecular weight between crosslink's (M_c), is studied. It was observed that with increasing the weight of the crosslinking agent, V_e , ρ_p and V_2 increased and M_{SD} , %swelling by volume decreased, but changes of M_c is erratic. **Keywords:** crosslinking time, crosslinking temperature, crosslinking density, crosslinking agent, swelling degree

INTRODUCTION

During the recent years, the use of the inorganic nanocomposite elastomer polymers has been highly focused on by the researcher as a scientific fascinating topic. Taking advantage of the inorganic fillers in this type of the polymers, the bulk characteristics and the mechanical resistance of such nanocomposites can be considerably enhanced. The imbalanced distribution of the pressure and the spoiled membranes surfaces can substantially degrade the bulk characteristics and the mechanical resistance of such nanocomposites.

PDMS can be used as an appropriate alternative in elastomer polymers due to its high resistance level, thermal and chemical stability, its excellent fraction ability and also contributing to the small molecules permeability features. The organic particles mass transfer from PDMS dense membranes is based on the solubility assumptions and permeating particles infiltration into the polymer [1-4]. Since PDMS has to be dissolved in non-aqueous oil based solvents, simultaneous making of the silicon precursors hydrolysis-condensation and PDMS oligomers cross-linking in a homogenous phase is impossible. Hydrolysis and condensation occur when the inorganic precursors and the catalyst and the induced particles meet in a common surface of the water and oil.

Polymers cross-linking in membrane-related technologies causes the membrane to become

insoluble in the aggregated feed and also it has been found to cause the membrane swelling be reduced and, consequently, makes the selectivity to be improved in respect to a certain particle. But, it may also cause a reduction in permeating particles infiltration to the membrane [5,6]. Changing the extent to which there is made use of the cross-linking agent mass, the PDMS-related swelling rate has been considerably changed [7-9].

The membrane strength to resist against swelling which results from the lattice-like spatial structure formation can be improved via making use of a cross-linking agent [10].

Also, by making use of a cross-linking agent the swelling related to the upper membrane layer can be reduced and bring about a condition for a better consistency and better adherence of the upper and basic layers in inconsistent composite membranes [11]. It has to be pointed out that additional use of the cross-linking agent should be avoided since it causes membrane fragility as a result of the related membrane dimensional stability deficit and consequently the membrane of concern will be lost of its necessary efficiency [12].

Also, the mobility of the constituents extant in the polymeric chain is reduced with the increase in the use of additional cross-linking agent and the intra-chain free space is decreased accordingly and it is worth mentioning that all such factors cause the smaller molecules not to be able to infiltrate and

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permeate into the related membrane's larger molecules[13-16].

Among the important and effective factors influencing the permeability of a particle in PDMS membrane besides the findings related to the swelling agent, one can point to the particles' pore infiltration in the composite membranes and the inhomogenous quality of the inorganic (silicon) filler lattice.[17]

The cross-linking degree can be determined by two parameters which are the cross-linking agent factor and the cross-linking time.[18]

Polymer aggregation is used as an essential technique for acquiring an optimized hydrophilic in a given polymer or a certain hydrophobe in a hydrophilic polymer and also by aggregation here we mean that no covalence bond is formed between the polymers. Now, for obtaining an ideal and optimized aggregation proportion we can make use of mixing an hydrophilic polymer with a hydrophobe one in different concentration ranges and measure the permeability and selectivity in respect to a certain specified particle[6].

Polymer aggregation can be classified into two general groups:

1. Homogenous aggregation, in which the two specified and determined polymers have perfect solubility capacity in molecular scale for all of the aggregation ratios.

2. heterogeneous aggregation, in which the two determined polymers lack the perfect solubility potential for the specified aggregation ratios and in fact the dissolved regions of a polymer in the polymeric chain are no longer observable and this is considered as a mechanical weakness for the thin membranes; furthermore, in processes in which pressure is applied as a driving force in separating special particles such a method of aggregation should not be used.[19-21]

One of the important methods which, to some extent, resolves the problems related to the PDMS polymer mechanical resistance both in terms of being easily producible and consistent with the environment and also from the perspective of the scientific and technical-structural issues is the use of the inorganic particles and components in a nano-size range within the PDMS chain and allowing for PDMS lattice to swell with the presence of water and catalyst in the inorganic particles (silicon precursors).[22-24]

However, an applied and principled study of the degree of PDMS polymer cross-linking effect on the inorganic particles transfer characteristics in membranes which can be used in nanofiltration processes is what seems to be missing from the study

literature. And the reason for such a scarcity of research in such a field can be related to PDMS membrane's selective and genuine layer being of an exact and precise nature in which it has not been completely and explicitly shown and it is merely used for commercial and industrial purposes.[17]

Two basic factors play roles in controlling the structure and intra-binding of the PDMS chains: one of them is the chemical agents and catalyst curing and the other is the use of optimum cross-linking temperature.[25]

Regarding the cross-linking temperature, the great majority of the researchers have come to a common conclusion of the ambient (room) temperature (25 °C)[26], but there are also reports indicating a temperature between 25-150 °C and the effect of choosing such temperatures on the PDMS chain intra-binding structure has not been obviously clarified yet.[27-29]

In the current study four kinds of the membrane including PDMS, blend of PDMS with PEG, blend of PDMS with PES and blend of PDMS with PAN are used. so, variation of crosslinking agent (PDMS)(1.5,3, 4.4,5.8 and 7.15wt%) upon crosslinking density (V_e), swelling degree (M_{SD}), %swelling by volume, density of membrane specimen (ρ_P), volume fraction of rubber phase (V_2) and number average molecular weight between crosslink's (M_C), is studied.

EXPERIMENTAL

Membrane material

Poly dimethylsiloxane oligomer (the viscosity was 5000 mpa.sec and the corresponding average molecular weight was around 40000, Aldrich, USA), polyethylene glycol (the corresponding average molecular weight was around 4000, BASF, Germany), polyether sulfone (the corresponding average molecular weight was around 58000, flakes, BASF, Germany), poly acryl nitrile (the corresponding average molecular weight was around 45000, Merk, Germany), polyvinyl pyrrolidone as pore former (K90, the corresponding average molecular weight was around 360000, Merk, Germany), N,N-Dimethyl acetamide as solvent for fabricated of support layer (Merk, Germany), dibutyltin dilaurate as catalyst (Fluka, Switzerland), ammonia as inducer (Merk, Germany), asymmetric polyester ultra-filtration membranes used as support (Plasma Chem GmbH, Germany), n-heptane as solvent (Romil, UK), span80 as surfactant (Merk, Germany), ethanol as auxiliary liquid (Merk, Germany) and De-ionized water as non-solvent was used in all the experiments.

Membrane preparation

Specified amount of Span 80 as a surfactant, crosslinking agent (PDMS)(1.5,3,4.4,5.8 and 7.15wt%), as well as PDMS and PEG polymers were dissolved in n-heptane at room temperature to make a homogeneous solution. The weight ratio between solvent and polymer is amount 5.5 and weight ratio between all polymers in this study is equal. Inducer aqueous solutions were suspended with a concentration of 1 molar (ammonia dissolved in a specified concentration of Tris-HCl buffer solution in neutral PH). then specified amount of the above aqueous solution was added into the oil solution under mechanical stirring. The Weight ratio between polymers, PDMS(crosslinking agent), dibutyltin dilaurate and Span 80 is 10/1/0.2/0.2. After stirring for 1 hour, specified amount of dibutyltin dilaurate was added in the oil solution. After de- bubbling , the solution was cast onto the support layer; the solution for the support layer was prepared by dissolving 15wt% of PES and 3wt% of PVP in DMAc. The homogeneous solution cast on asymmetric polyester ultra-filtration membranes was immersed immediately in distilled water for remove the remaining DMAc. The membranes were first dried in air for 48 hours and then thermally annealed at 70°C (crosslinking temperature) for one hour(crosslinking time) to accomplish Cross-linking and evaporate the residual solvent. After that, the membranes were washed by De-ionized water and finally placed between sheets of filter paper and dried. All samples were stored in a dust free and dry environment before the performance of membranes were measurements.

Another set of samples was done in parallel using the same procedure, except that PEG omitted from medium and replace with PES and PAN membranes.

BASIC PRINCIPLE

Swelling measurements are often used to measure the crosslink density of PDMS. the degree of swelling (the amount of solvent imbibed) is known to be dependent upon the crosslink density of polymer (PDMS , blending PDMS with PEG, blending PDMS with PES and blending PDMS with 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 [29]:

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

The cross-linking density was measured by equilibrium swelling method.

cross-linking density was the calculation by the following Flory–Rehner equation [30]:

$$v_e = \frac{[\ln(1-v_2) + v_2 + \chi v_2^2]}{v(v_2^{0.333} - \frac{v_2}{2})} \quad (2)$$

Where: v_e was the cross-linking density of the polymer (mol/cm³); v_2 was the volume fraction of polymer phase; v was the molar volume of solvent (cm³/mol); χ was the interaction parameter between the polymer and the solvent. [30]

$$v_2 = \frac{\frac{m_1}{\rho_1}}{(m_2 - m_1)/\rho_2 + (m_1)/(\rho_1)} \quad (3)$$

Where m_1 and m_2 were the weights of the dried and swollen composite membranes, respectively; ρ_1 and ρ_2 were the density of composite membranes and the solvent . at room temperature, the membranes were weighed before immersed in heptane. after 48 hours the swollen membrane was taken out from the solvent solution and was then wiped by tissue paper to remove the residual heptane before weighed.

The polymer-solvent interaction parameter (χ) was determined from the Bristow and Watson semi-empirical equation [31]:

$$\chi = \left(\frac{V_s}{RT}\right)(\delta_s - \delta_p)^2 \quad (4)$$

V_s is the molar volume of solvent, R is the universal gas constant, T is the absolute temperature, δ is the solubility parameter and subscripts 's' and 'p' refer to the solvent and polymer, respectively.

The solubility parameter of PDMS, PEG, PES, PAN and solvent are 21.01($\frac{j}{\text{cm}^3}$), 20.1($\frac{j}{\text{cm}^3}$), 18.5($\frac{j}{\text{cm}^3}$), 26.61($\frac{j}{\text{cm}^3}$) and 15.3 ($\frac{j}{\text{cm}^3}$) respectively, according to the data taken from polymer handbook. [32]

$$\delta_p = \sum x_i \delta_{pi} \quad (5)$$

Index 'i' in the above relation is related to the constituent polymer in each of the membranes, for instance in producing PDMS + PEG composite membranes, The solubility parameter belonging to PDMS and PEG should be inserted into the relation and the weight component value (x) should be set to 0.5 for each of the polymers due to their identical difference ratios, The only exception is used for the time that there is just made use of PDMS polymer for producing membrane in which state 'x' is set to 1 and the only solubility parameter taken to consideration here is the one related to PDMS.

$$M_c = \frac{\rho_p}{v_e} \quad (6)$$

M_c is the number average molecular weight between crosslink's (physical); ρ_p is the density of the polymer and v_e is the crosslinking density. [30]

Density measurements using the hydrostatic weighing method. The membrane density (ρ_p) was calculated by [33,34]:

$$\rho_p = \frac{m_1}{m_1 - m_L} \times \rho_0 \quad (7)$$

Where m_1 is weight of dry membranes, m_L is the weight of membranes in the auxiliary liquid and ρ_0 is the density of the auxiliary liquid. For the determination of the density of PDMS, blending of PDMS with PEG, blending of PDMS with PES and blending of PDMS with PAN membranes, ethanol was used as the auxiliary liquid.

Eq.(8) is approximately equivalent with Eq.(1) except which Eq.(1) basis of volumetric scale. m_1, m_2 definition same parameters in Eq.(3).

swelling degree (M_{SD}) of the composite membranes was then calculated by:

$$M_{SD} = \frac{m_2 - m_1}{m_1} \times 100 \quad (8)$$

RESULT AND DISCUSSION

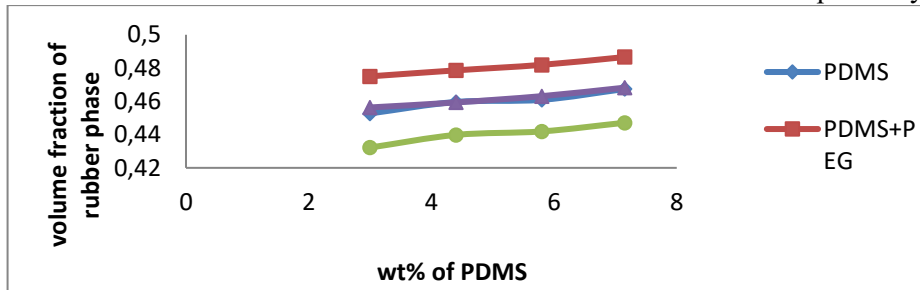


Fig. 1. Variation of volume fraction of rubber phase with wt% of crosslinking agent

Fig.1 is illustrative of the volume fraction of rubber phase with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure, the volume fraction of rubber phase increases linearly with the increase in the extent to which PDMS is consumed, as a cross-linking agent [35]. According to the Eq.(3), with the increase in PDMS consumption rate in producing similar composite membranes, m_1 and ρ_1 both increases but

in this research ,a variation of the cross- linking agent (PDMS) upon cross- linking density (V_e),swelling degree (M_{SD}),%swelling by volume, density of membrane specimen (ρ_p),volume fraction of rubber phase(V_2) and number average molecular weight between crosslink's (M_C),is studied. in this research usage a blend of polymers that are comprised of PDMS, PEG, PES and PAN as polymers, asymmetric polyester ultra-filtration membranes used as support with crosslinking PDMS as cross- linking agent, PVP as pore former, ammonia as inducer ,dibutyltin dilaurate as catalyst and span 80 as surfactant.

For fabricated all of the composite membrane, crosslinking temperature and crosslinking time are fixed and 65c and 1 hour respectively.

due to the presence of ρ_1 both in the numerator and denominator parts the effects exerted by such a parameter is somehow neutralized and the $m_2 - m_1$ part is reduced in the end.

Now if we consider the effect of the parameters altogether, then it is observed that with the increase in PDMS consumption rate, v_2 is also increased. The method of obtaining ρ_1 has been given in the Eq.(7).

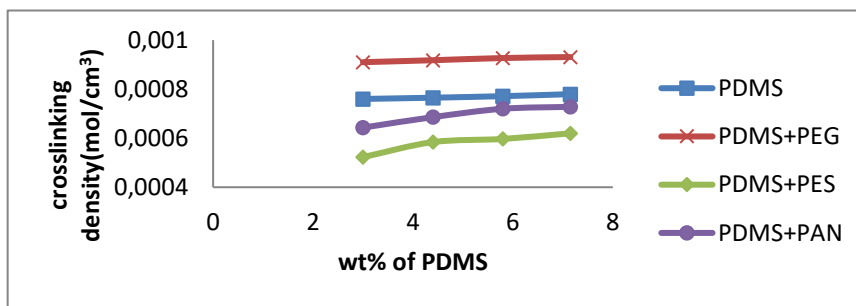


Fig. 2. Variation of crosslinking density with wt% of crosslinking agent.

Fig.2 is illustrative of the composite membranes cross-linking density with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure, the cross-linking density increases linearly with the increase in the extent to which PDMS is consumed [35]. As it was mentioned previously, corresponding to the Eq. (3) v_2 increases with the increase in PDMS consumption rate, now

according to the Eq. (2), with the increase in v_2 and v being fixed v_e increases consequently. Also, based on the figure, it can be seen that the highest increase in the cross-linking agent density with an increase in PDMS consumption rate belongs to PDMS + PEG composite membrane and the main reason which can be emphasized here as the factor contributing to the emergence of such a phenomenon is that

corresponding to the Eq. (3), the highest value of v_2 has been seen for PDMS + PEG polymeric mixture as a consequence of which and according to

the Eq. (2), the highest value for v_e has also been obtained for the same composite membrane.

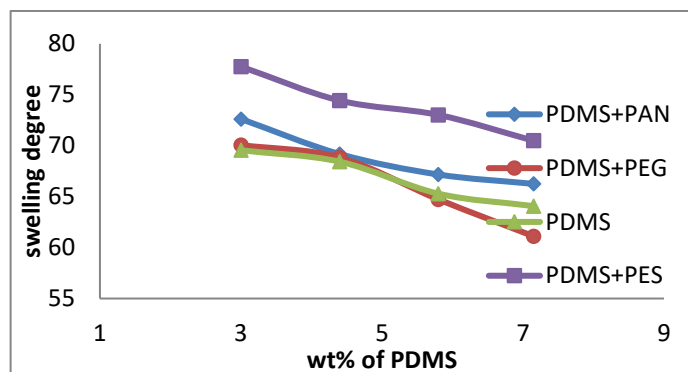


Fig. 3. Variation of swelling degree with wt% of crosslinking agent.

Fig.3 is illustrative of the swelling degree with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure, the swelling degree decrease linearly with the increase in the extent to which PDMS is consumed. [35]

According to the Eq. (8), with an increase in PDMS consumption rate, the similar composite

membranes m_2 and m_1 both increase, but they generally result in M_{SD} reduction. But, in various composite membranes, this is the m_2 parameter which plays a part in as an effective factor. That is because m_1 stays the same for all of the composite membrane.

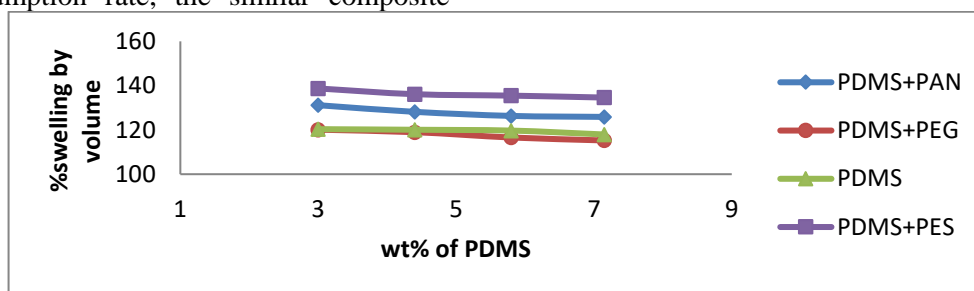


Fig. 4. Variation of %swelling by volume with wt% of crosslinking agent.

Fig.4 is illustrative of the % swelling degree by volume with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure, the %swelling by volume decrease with the increase in the extent to which PDMS is consumed. [35]

According to the Eq.(1), with the increase in

PDMS consumption rate in producing similar composite membranes, the specific gravity of the solvent remains fixed, but the rest of the expressions existing in the relation all undergo an increase which generally causes the % swelling by volume of the related composite membranes to reduce

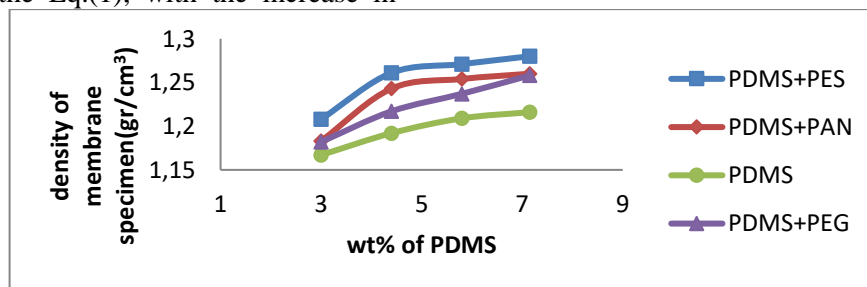


Fig. 5. Variation of density of membrane specimen with wt% of crosslinking agent.

Fig.5 is illustrative of the density of membranes with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure,

the density of membranes increases with the increase in the extent to which PDMS is consumed.

According to Fig.5, the highest density pertained

to PDMS + PES composite membranes. Among such composite membranes, PDMS + PAN have the highest m_L in contrast to the rest of the composite membranes, The same reason causes these

composite membranes to enjoy the highest density, And According to the polymer producer data, the highest density of the extant polymers can be seen to be belonging to PES.

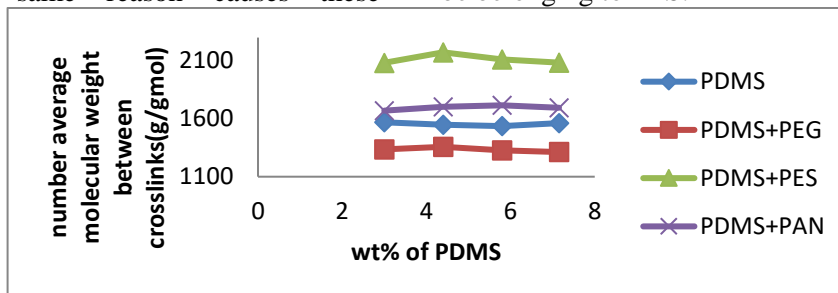


Fig. 6. Variation of membrane average molecular weight between crosslink's with wt% of crosslinking agent.

Fig.6 is illustrative of the number average molecular weight between crosslink's with a wt% of the cross-linking agent consumed in the composite membranes. According to this figure, the number average molecular weight between crosslink's changed erratic with the increase in the extent to which PDMS is consumed. It has to be pointed out that among the existing polymers; PES possesses the highest ρ_p and the lowest v_e . The same mentioned dual factors cause the PDMS + PES membrane polymer to become in possession of the highest M_c .

Fig.6 shows the change of number average molecular weight between crosslinks with wt% of the crosslinking agent for fabricated of membranes. According to this figure, with increased the weight of crosslinking agent, the number average molecular

weight between crosslink's of membranes is decreased.

According to by Eq. (5), with increasing the weight of crosslinking agent for fabricated of membranes, ρ_p is increased and v_e is decreased; as a result number average molecular weight between crosslinks is decreased.

SEM observation

Cross-sectional morphology of the Nanocomposite membrane probed by SEM is shown in Fig.7. As it can be observed, two different layers can be distinguished. The dense, tight and nonporous morphology of the top layer supplied its function as the basis of selectivity. Besides, the macro void with the channel like the structure of the support layer was proper to the convenient flux of the permeate.

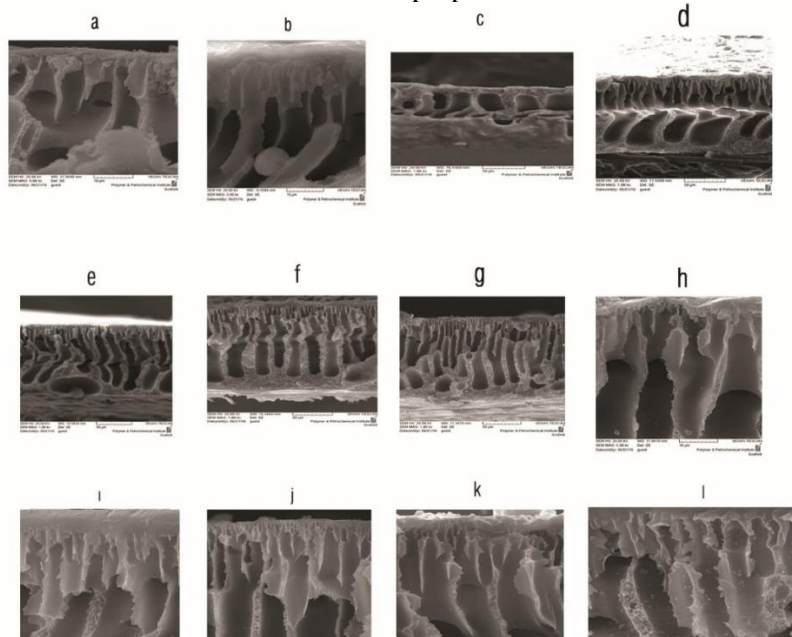


Fig.7: Cross-sectional SEM images of composite membranes: **a:** PDMS, 1.5wt% PDMS, **b:** PDMS, 3wt% PDMS, **c:** PDMS+PEG, 3wt% PDMS, **d:** PDMS+PEG, 4.4wt% PDMS, **e:** PDMS+PES, 3wt% PDMS, **f:** PDMS+PES, 4.4wt% PDMS, **g:** PDMS+PES, 5.8wt% PDMS, **h:** PDMS+PAN, 1.5wt% PDMS, **i:** PDMS+PAN, 3wt% PDMS, **j:** PDMS+PAN, 4.4wt% PDMS, **k:** PDMS+PAN, 5.8wt% PDMS, **l:** PDMS+PAN, 7.15wt% PDMS

Comparing the Fig.7a and Fig.7b it can be seen that with the increase in PDMS consumption rate in producing the relevant composite membranes, the membrane density is somehow increased. Also, the Fig.7c and Fig.7d and/or Figs.7e,f and Fig.7g can be compared. Comparing the fig.7h to fig.7l it can be observed that similar to the figures related to the above-mentioned composite membranes, with the increase in PDMS consumption rate, the density is increased and the membrane-cross-linking agent intra-structure coherence becomes more stabilized and firmer and this is suggestive of the idea that the cross-linking density pertaining to the composite membranes is also increased.

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. In this research, the effect of the crosslinking agent (PDMS) upon crosslinking density (V_e), swelling degree (M_{SD}), % - swelling by volume, density of membrane specimen (ρ_P), volume fraction of rubber phase (V_2) and number average molecular weight between crosslink's (M_C), is studied. It was observed that with increase weight of the crosslinking agent, V_e , ρ_P , and V_2 , is increased and M_{SD} and %swelling by volume is decreased but changes of M_C is erratic.

According to Fig.3 and Fig.4, Due to the synergistic effect between the polymers, blending of PDMS and PEG has minimum swelling degree (61.11) and % swelling by volume (115.24%), it means, this blending have good selectivity for special spice. It is expected that the current study will devote a novel method for the rational design and facile fabrication oleophilic polymer- based polymer-inorganic nanocomposite membranes to better meet the diverse application requirements.

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