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Morphological Study of Polyimide Mixed Matrix Membranes

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ABSTRACT

Polyimide mixed matrix membranes (MMMs) were synthesized by incorporating different fillers of zeolite 4A,
carbon molecular sieve, and homemade carbon nanotubes into Matrimid 5218 and P84 via solution casting method.
MMMs were characterized by Scanning Electron Microscopy (SEM), Differential Scanning Calorimeter (DSC) and
Thermo Gravimetric Analysis (TGA). Effects of fillers loading and polymer concentration on MMMs structure and
thermal treatment on removing MMMs probable defects were investigated. The experimental results showed that
filler particle size, nature and polymer concentration have significant effects on filler distribution inside the polymer
matrices. Incorporation of fillers inside the polymers resulted in polymer free volume reduction and polymer chain
attachment to and/or entrance into fillers pores and more glassy (brittle) MMMs as can be concluded by DSC and
TGA analysis. Thermal treatment was found as an effective method for removing probable defects inside the
MMMs.

Keywords: Mixed matrix membrane, polyimide, filter size and nature, polymer concentration, thermal treatment,
morphology

1.0 INTRODUCTION

Membrane based separation processes are fast
developing in current existing and for coming
industries. Membrane materials need to be
modified to fully and economically exploit
available opportunities. High stability, permeation
flux and selectivity at low production cost are
always the most important criteria when
developing a membrane for a specific application

[1]. Many efforts are being carried out to modify
current membrane materials. Ion exchange is a
method for improving separation performance of
zeolitic membranes[2-3]. Others are Crosslinking,
grafting and blending which were also applied for
polymeric membranes [4-8]. Due to the membrane
material unique characteristics, researchers are
seeking for new approach to employ desired
properties of fine inorganic particles incorporated
in polymers to form a so called "Mixed Matrix
Membranes (MMMs)." Therefore, the new
generation of membrane researchers are trying

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to employ desired properties of fine particles and polymers while omitting their undesired properties [9-11].

Proper polymer and filler selection, preparation and post-treatment procedure are of the most important key features in successful MMMs preparation [9, 11]. Filler size, content and polymer concentration are among the affecting parameters on filler distribution inside polymer matrix and MMMs separation performance [11-13]. Many researches have been focused on rubbery polymers with high affinity to fillers and there are approximately good connections between polymer and filler phases [9, 14]. Glassy polymers exhibit higher separation performance with regard to rubbery polymers and at the same time have higher rigidity in nature and they are hard to incorporate with inorganic fillers [11, 14]. Void formation around the incorporated fillers, fillers pores blockage by polymers and chain rigidification are undesired phenomena that can potentially occur in MMMs preparation especially for glassy polymers and these result in MMMs morphology to be apart from ideal morphology [9-11, 15]. Different morphologies may be observed in MMMs as shown schematically in Figure 1 [9].
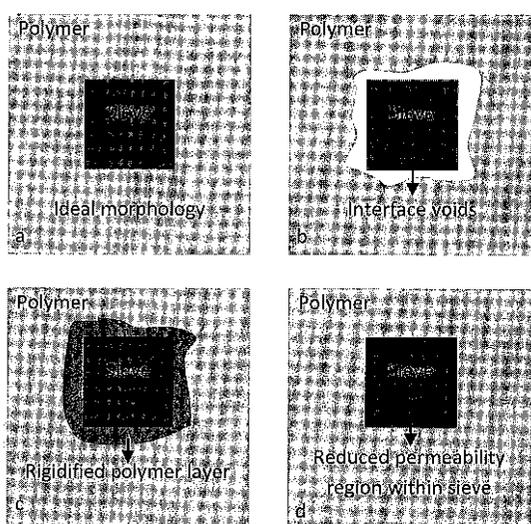

Figure 1   Ideal and different non-ideal cases may be encountered in MMMs preparation [9]

Similar to that mentioned in literature by Jiang *et al.* [12], a synthesis procedure was employed to study the effects of synthesis parameters on MMMs structure [9, 11-12]. Objective of this study was to develop defect-free MMMs using glassy polyimides of Matrimid 5218 and P84 and zeolite 4A, carbon molecular sieve and homemade carbon nanotube (CNT) as fillers. Polyimides have high glass transition temperatures, T_g, and exhibit excellent thermal stability. Glassy polymers of Matrimid 5218 and P84 have glass transition temperatures of ~ 300 and 315°C, respectively and are reasonably chemically stable in most organic solvents and weak acids [11].

2.0   EXPERIMENTAL

2.1   Materials and Equipments

Matrimid 5218 was purchased from Huntsman Chemical Company, USA. P84, zeolite 4A and carbon molecular sieve (CMS) were dedicated by HPPolymerCo.,Iran Research Institute of Petroleum Industries and Activated Carbon Business Divisions, Japan EnviroChemical, respectively. Normal Methylpyrrolidone (NMP,≥ 99.5%) was purchased from Merck Chemicals Co. as solvent and used as received. Some glass plates and holder meshes were fabricated in order to prepare MMMs. A vacuum oven (Wisd, WiseVen), an oven (Memmert), some stirrers (FALC, F20, Italy) and a digital microbalance (Percisa, 310 M) were also used. A programmable oven was also used to thermally treat the MMMs.

2.2   Preparation of MMMs

Polymer powders and filler particles were activated over-night at 120°C under vacuum to remove any adsorbed impurities. After activation, the filler was suspended in the solvent and stirred for about 24 h at room temperature and then the polymer was added and stirred at room temperature for the next 24 h. The as-prepared solution was cast onto a glass plate after degassing in vacuum for 4 h followed by solvent evaporation at 170°C for about 2 h. The nascent membranes
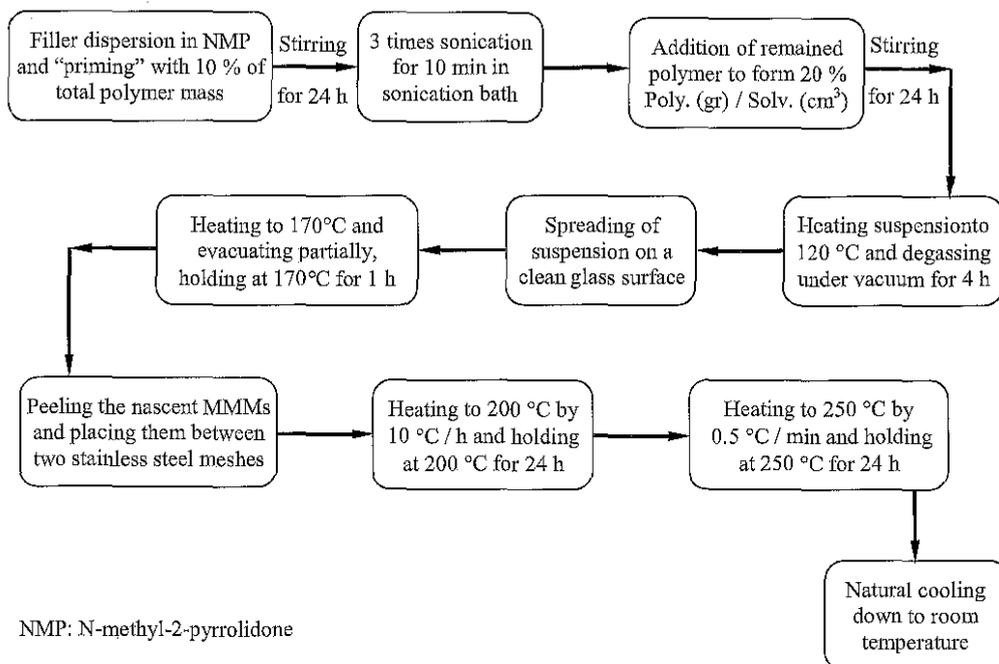
Figure 2   Modified MMMs preparation procedure based on L. Y. Jiang *et al.* [12]

were then heated inside the oven for 2 h, the membranes were peeled off from the glass plates, and put in between two wired stainless steel meshes individually to balance heat transfer from top and bottom of each membrane. As a result, the solvent at the bottom side of the membrane could be removed more efficiently, and the membrane could be more homogeneous [12]. Later, the membranes were hold at about 200°C overnight to fully remove the solvent. The membranes were further annealed at a rate of 0.5°C/min to 250°C and remained for 12 h. This step could also help removing the residual solvent. The MMMs were finally allowed to be cooled naturally down to room temperature. Thickness of the membranes was in the range of 35-60 μm as measured by a Mitutoyo micrometer (accuracy of 1 μm). The process was based on Ying Jiang *et al.* [12] procedure with a little difference as reported in Figure 2.

2.3   Membranes Characterization

Geometrical characteristics and morphology of the MMMs were observed using a VEGA\\TESCAN SEM. The samples were prepared by fracturing in liquid nitrogen then coated with Au. Glass transition temperatures, T_g, of the neat polymeric membranes and MMMs were measured using a Perkin Elmer-Pyris6 DSC with heating and cooling rates of 10°C/min under nitrogen environment up to 600°C. Perkin Elmer-Pyris diamond TGA was performed in order to evaluate thermal stabilities of the prepared MMMs and the neat polymeric membranes. The samples were heated circularly from 30 to 600°C with heating rate of 10°C/min under nitrogen environment.

3.0   RESULTS AND DISCUSSION

3.1   SEM Studies

Cross section of the neat Matrimid membrane is shown in Figure 3. Nano-sized (~ 10 nm) aerosil silica was dispersed inside P84 (10 wt.%). Particles were be agglomerated (~ 5 μm) and partially sedimented into the MMM due to the gravitational force (Figure 4, a). As observed, the agglomerated particles tend to move to the lower surface of the MMM (Figure 4, b) and the density of aerosil silica particles is less in the upper surface. Different precaution efforts including sonication before casting to dissociate aggregated particles [16] and using more concentrated suspensions to partially balance gravitational force [9, 12], were performed.

Larger 4A zeolite particles (300 - 500 nm as reported by the dedicator) was incorporated into Matrimid 5218 (10 wt.%). The particles were aggregated again but there was more uniform filler distribution as observed in Figure 5. Top surface and cross section SEM images show better distribution of zeolite 4A than that of silica aerosil. There is greater buoyant force and as a result less sedimentation occurs. Generally, fillers sedimentation in MMMs is inevitable since there are nearly large density difference between inorganic fillers (typically 1.3 gr/cm^3) and solvents (typically 0.9 gr/cm^3). Larger fillers (micro-sized) results in slightly better distribution as shown in Figure 6 for CMS - Matrimid 5218
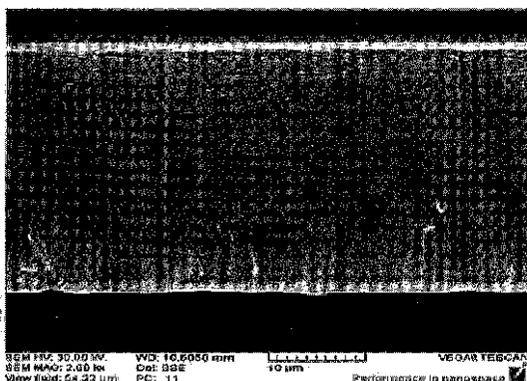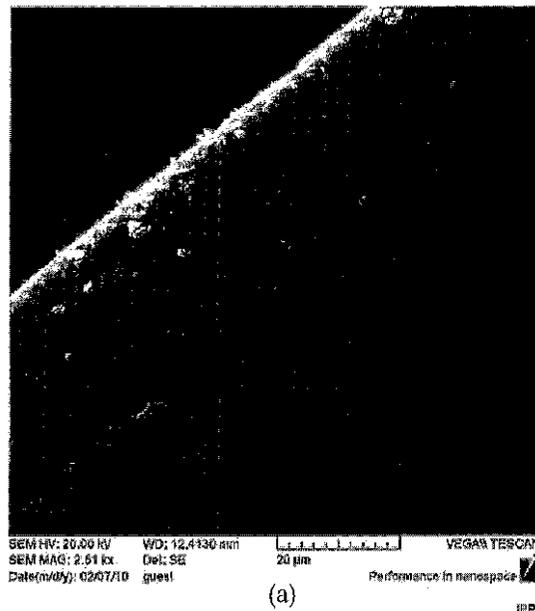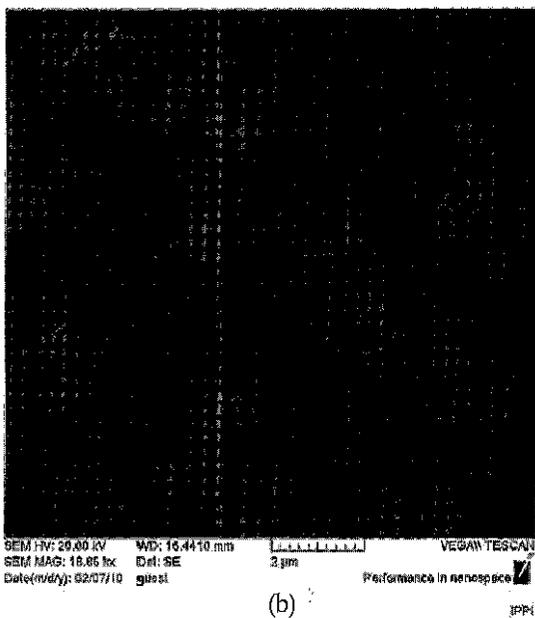

**Figure 3**   Cross-sectional SEM image of the neat Matrimid 5218 membrane
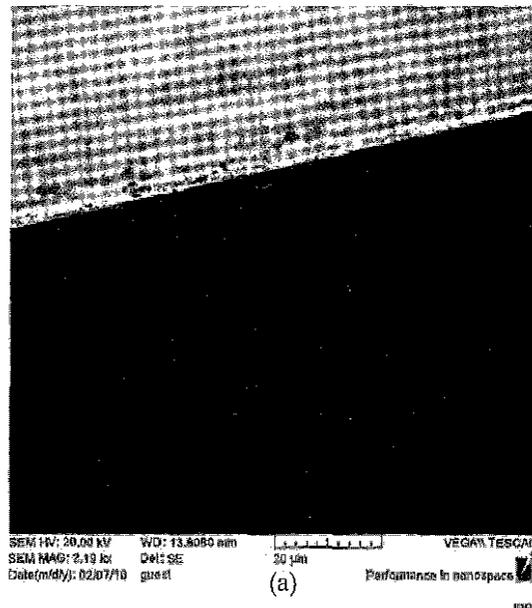

(a)

(b)

Figure 4   SEM image of 10 wt.% aerosil silica - Matrimid 5218 (10 wt.%) MMM, average thickness of 35 μm, (a) cross section, (b)lower surface
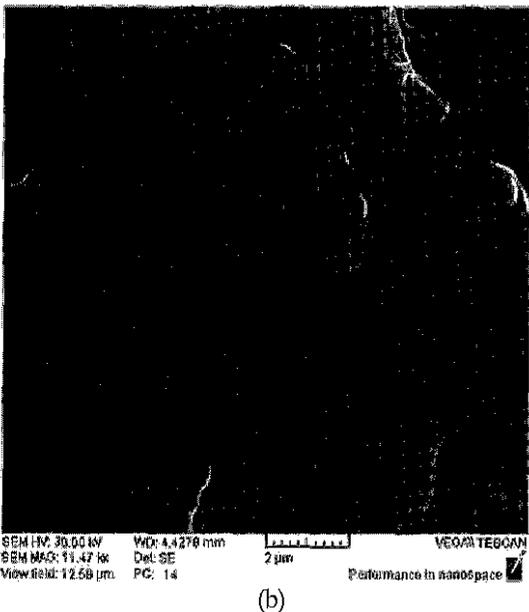
(10 wt.%). Since CMS has lower density and larger volume, it is affected by greater buoyant force and more uniform filler distribution is obtained. However, in separation point of view,
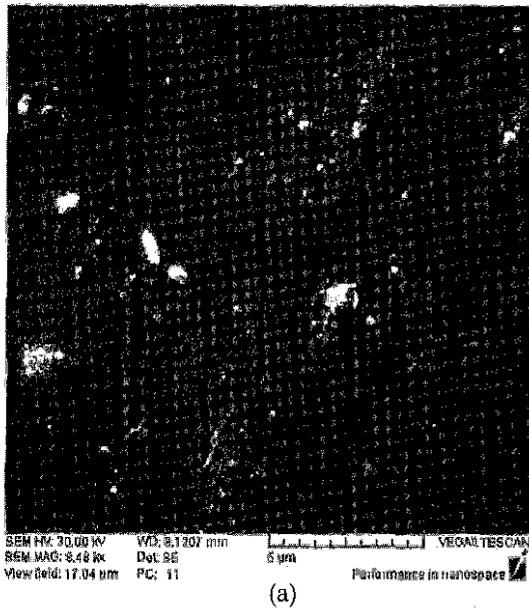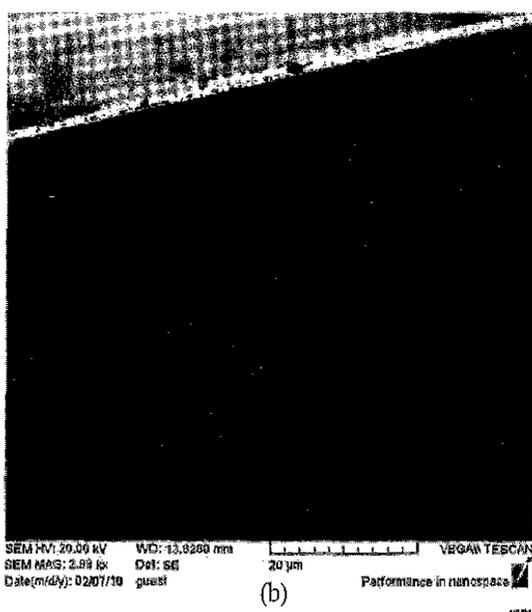
Figure 5 SEM image of 10 wt.% zeolite 4A - Matrimid 5218 (10 wt.%) MMM, average thickness of 45 μm, (a) top surface, (b) cross section

Figure 6 Cross section SEM image of 10 wt.% CMS - Matrimid 5218 (10 wt.%) MMM, average thickness of 45 μm

incorporation of smaller particles results in better performance [9, 17].

As mentioned above, concentration (viscosity) of the casting solution to form MMMs, is one of the main affecting parameters on the filler distribution within the MMMs structure [9, 12]. More concentrated (viscose) solutions were employed to prepare MMMs and the results
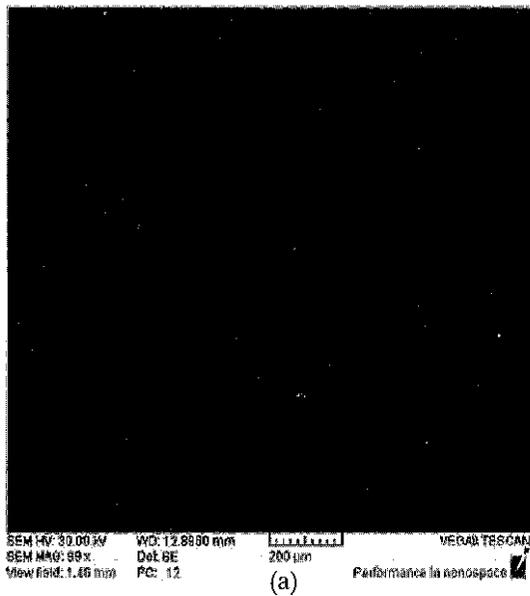
(a)

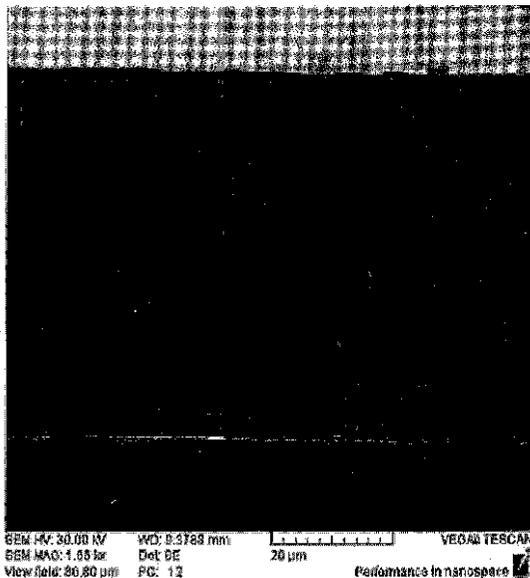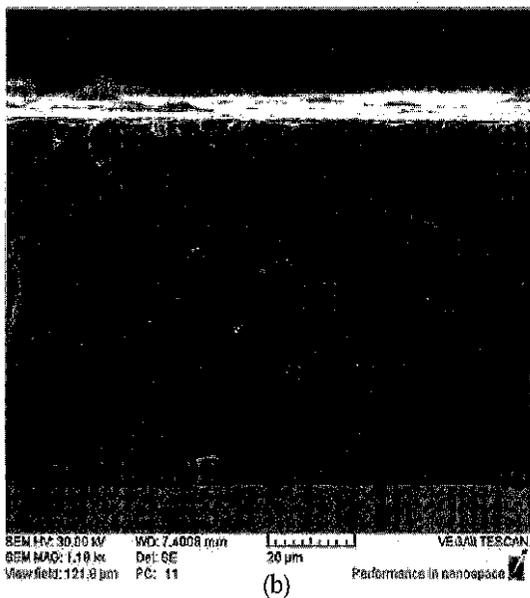**Figure 8** Top SEM image of 5 wt.% zeolite ZSM-5 - Matrimid 5218 (15 wt.%) MMM, average thickness of 55 μm

(b)

Figure 7 SEM image of 5 wt.% zeolite ZSM-5 - Matrimid 5218 (15 wt.%) MMM, average thickness of 55 μm, (a) top surface, (b) cross section

Figure 9 Cross section SEM image of 5 wt.% CMS - P84 (15 wt.%) MMM, average thickness of 50 μm

showed more uniform distribution of the filler, as indicated in Figure 7 (a and b) for zeolite ZSM-5 (5 wt.%)- Matrimid 5218 (15 wt.%) MMM. Nearly a uniform filler distribution is observed in cross section, indicating the effectiveness of solution concentration (viscosity) on the filler distribution.

Better connection between filler particles and polymer is also observed in more concentrated (viscose) solutions as reported in Figure 8 for the ZSM-5 (5 wt.%) -Matrimid 5218 (15 wt.%) MMM.

The same behavior is observed in the case of micro-sized CMS dispersed in a more viscose solution (Figure 9).

3.2 DSC and TGA Studies on Prepared Membranes

As inorganic filler is incorporated inside a polymer matrix, the end chains of polymer molecules may be attached to the inorganic filler particles surface by chemical (or hydrogen) bonding, or entered to the pores of filler particles. In both cases, the polymer chains in a certain region around the filler particles are rigidified and this results in restriction of polymer chains movement (Figure 1,c and d) [9, 18-19]. Zhang *et al.* employ edcalcined and uncalcined ZSM-5 and observed that polymer chains entrance doesn't occur in the case of uncalcined ZSM-5 which is plugged by a template. They concluded that the presence of mesopores is a key parameter to achieve a good contact [19]. Although the good contact may be observed in such cases, chaotic polymer chains entrance into filler particles may result in smaller aperture for penetrants and abortiveness of fillers [20].

DSC analysis of granular Matrimid 5218 showed T_g of 297°C as indicated in Figure 11. The neat Matrimid 5218 membrane was also investigated using cyclical DSC and its T_g was found to be 291 ÚC (Figure 12). The deviation can be related to the different analytical equipments. The prepared MMMs were also investigated using DSC analysis. The results showed that incorporation of fillers inside polymer matrices increases T_g of the MMMs compared with these of the neat polymeric membranes due to the filler polymer chains interactions. The interactions can be in form of physical or chemical bonding to the filler surface or polymer chain entrance into the filler pores. T_g values of the MMMs are reported in Table 1. By adding more filler, free volume of polymer reduces since it is occupied by the filler and some rigidified regions appeared in the neighborhood of filler particles [12, 19]. In other words, the incorporated filler particles restrict movement and alignment of the polymer chains around the filler
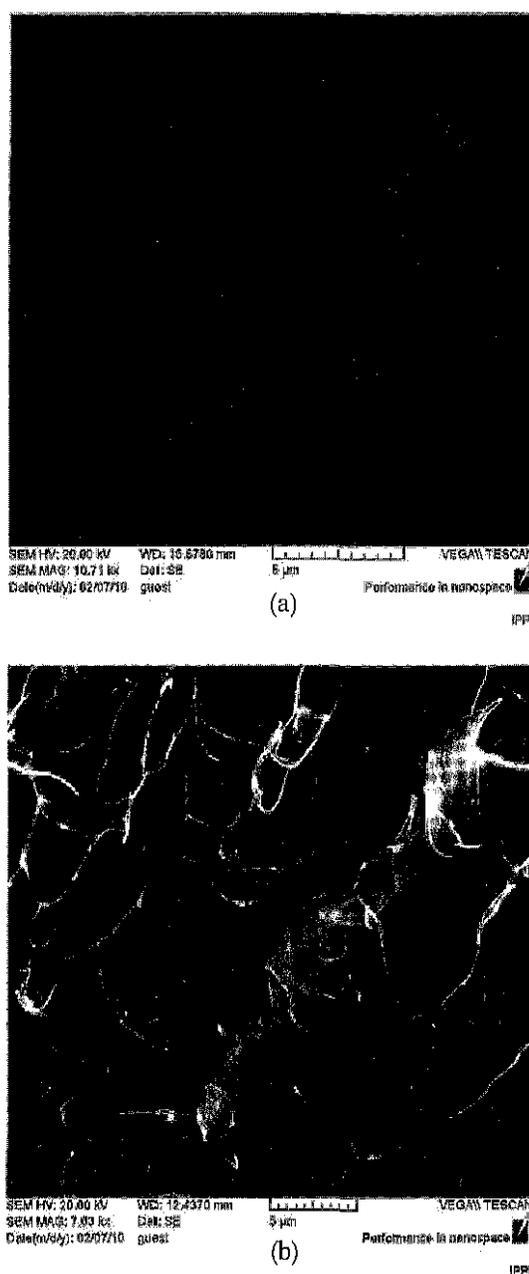

(a)

(b)

Figure 10 Cross section SEM image of 5 wt.% CMS - P84.(15 wt.%) MMM, average thickness of 50 μm

and this causes T_g value to increase [1]. The results showed that incorporation of zeolite 4A results in more brittle MMMs and this can be attributed to its tough nature. As zeolite 4A content increases, glassier MMM with higher T_g
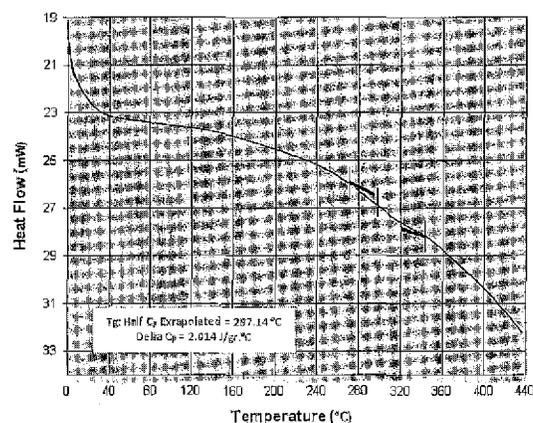
Figure 11   DSC analysis of the granular Matrimid 5218

Table 1   DSC analysis of the granular Matrimid 5218

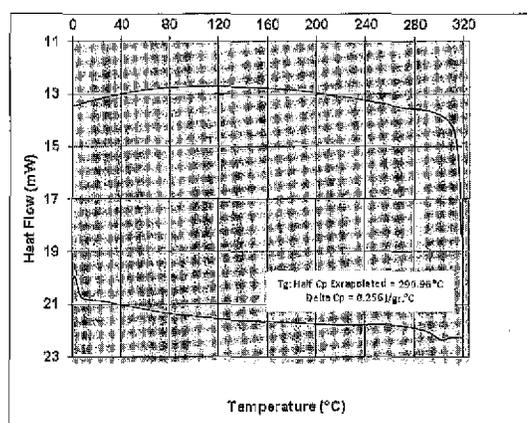| Polymer (wt.% in NMP)	Filler (wt.%)	T_g (C)
Matrimid5218 (10)	zeolite 4A (5)	298
Matrimid5218 (10)	zeolite 4A (15)	306
Matrimid5218 (10)	CMS (10)	296

Figure 12   DSC analysis of the neat Matrimid 5218 membrane

is obtained due to the more filler-polymer chains interactions. CMS is softer than zeolite 4A and as a result MMMs containing CMS are more flexible and their T_g values are lower.

The prepared membranes were also studied using TGA for their thermal stabilities. The neat Matrimid 5218 (10 wt.%) membrane and zeolite 4A (5 and 15 wt.%) and CMS (15 wt.%) - Matrimid 5218 (10 wt.%) MMMs were studied. The results (Figure 13) showed that after 500°C, thermal stabilities of the MMMs are higher than that of the neat membrane (weight losses of the

neat Matrimid 5218 (10 wt.%) membrane and zeolite 4A (15 wt.%) - and CMS (15 wt.%)-Matrimid 5218 (10 wt.%) MMMs were recorded as 34.51, 32.23 and 27.86%, respectively). Higher thermal stabilities of the CMS-Matrimid 5218 MMM may be due to the large pore aperture of CMS (~ 50 Å, as reported by the manufacturer) and the more polymer chains entrance to CMS pores. Also, there are larger rigidified regions around and inside the fillers [18], while CMS nature is softer than zeolite 4A. The analysis showed connections formed between the polymers and the fillers, while rigid glassy polymers were employed. As observed, as filler content in MMMs increases, their thermal stabilities increase as indicated in Figure 14 for 5 and 15 wt.% of zeolite 4A in Matrimid 5218 MMMs. Incorporation of more fillers results in higher filler-polymer chains interactions and more rigidified regions in the MMMs.

3.3 Effects of Annealing

Non-ideal morphologies as explained above are inevitable in most cases. However, some precautions and/or treatment processes should be considered in order to prevent formation of these defects and/or remove them. The main defect in MMMs structure, especially for those of glassy polyimides, is detachment of the polymer chains from the filler surface and void formation around
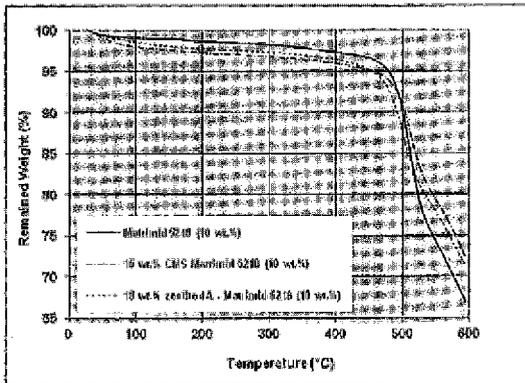
Figure 13 TGA analysis of the prepared neat and MM Matrimid 5218 membranes
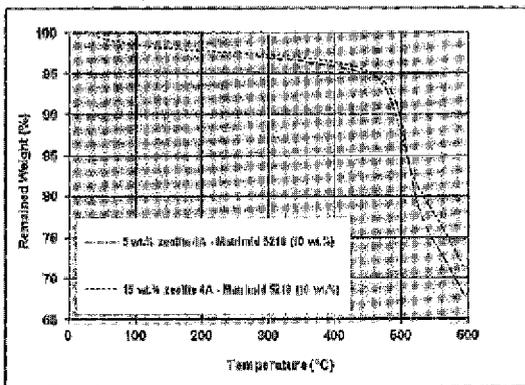

Figure 14 TGA analysis of the prepared of zeolite 4A (5 and 15 wt.%) - Matrimid 5218 (10 wt.%) MMMs

the filler particles. One of the most effective post-treatment processes that can remove the voids around the filler particles is to perform thermal treatment on the prepared MMMs at temperatures around their T_g values. This enhances polymer chains mobility and allows the remained stresses or drying stresses to be annealed and an integrated MMM to be formed. In the current study, some homemade CNT [21] (10 wt.%) - P84 (10 wt.%) MMMs were prepared to investigate thermal treatment effectiveness on removing the probable defects. Investigation of the MMMs before and after thermal treatment are based on Jiang et al. [12] procedure. The results from SEM images (Figure 15), showed that thermal treatment could effectively repair the probable defects which were the results of shrinkage or residual drying stresses.
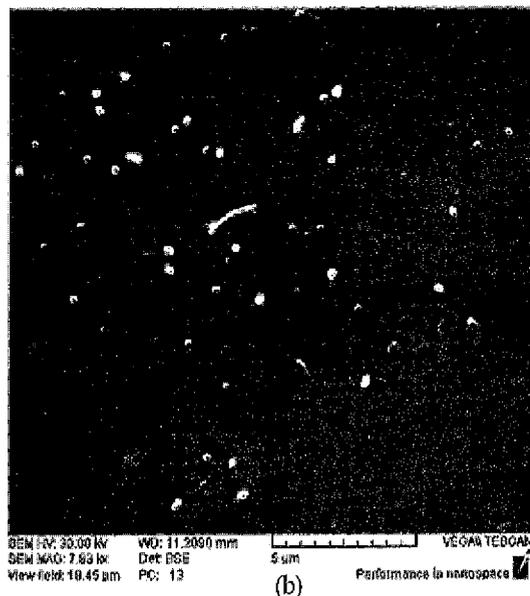

(a)

(b)

Figure 15 Cross sectionSEM image of 10 wt.% CNT - P84 (10 wt.%) MMM, average thickness of 55 im, (a) as dried at 80 °C and 1 bar, (b) after thermal treatment viathe procedure based on Jiang et al. procedure[12]

4.0 CONCLUSION

In this study, zeolite 4A, CNT and CMS- Matrimid 5218and P84 MMMs were fabricated. Some affective variables were investigated on MMM formationusing SEM, DSC and TGA analysis. Size and density of fillers were found to have strong effects on their distribution within the polymer matrices. Polymer solution concentration (viscosity) was found as another effective variable on fillers distribution within MMMs structure. Incorporation of fillers inside polymers resulted in higher T_g and thermal stabilities of MMMs as compared with those of neat polymeric membranes due to polymer chains attachment (and consequently rigidification) and/or chains entrance into filler pores. Nature and content of fillers were also found as the most determining variables. Thermal treatment was found as an effective solution for removing probable defects in MMMs structure. Effects of different parameters on MMMs structure and their separation performance are under investigation.

ACKNOWLEDGEMENT

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