CHAPTER 5

Synthesis and Characterization of PIMs

5. Synthesis and Characterization of PIMs

5.1 Challenges associated with membrane synthesis

PIMs with different compositions were prepared at various temperatures to find out its optimum synthesis temperature. Keeping the boiling point of THF in mind, the upper limit of synthesis temperature was set to 46 °C. In between 42-46 °C, the major part of the solvent gets evaporated in mixing phase. Therefore, the amount of solution was not sufficient for pouring it into a petri dish. In fact, this was the case for all sets of composition for the temperature above 36 °C. Even though the solution was found to be sufficient for pouring once the temperature was maintained in the range of 30-36 °C, the difficulty emerged during the peeling off membrane phase due to the membrane thickness. The membranes were found to have non-uniform thickness, uneven surface and not fully transparent in some case where temperature was less than 23 °C. The reason behind the above-mentioned problems may be attributed to the non-uniform evaporation of solvent. Therefore, authors concluded that the higher membrane synthesis temperatures may cause faster evaporation of solvent and the lower temperature causes the irregular evaporation, which eventually leads to the non-uniform thickness, uneven surface, and loss of transparency. The solvent evaporation rate and thickness of the PIMs will decide the characteristics and distribution of carrier in the PIMs (Abdul-Halim et al., 2013). Figure-5.1 shows optical images of synthesized PIMs at different temperature. Considering all these challenges, the optimum synthesis temperature for PVC/ACORGA M5640 PIMs is found to be in the range of 25-30 °C. Besides temperature, moisture content during synthesis, either coming from inefficient washing and drying of the glass wares or from the atmospheric moisture, act a critical role in final texture of the membrane. In this situation, even if mixing of components will look fine, yet after the evaporation of solvent membrane may have some of the major and minor holes and it is very brittle in nature as can be seen in figure-5.2. Therefore, all the glass wares used during the experiments should be oven dried and the pouring of solution should be at dry places in order to avoid these issues.

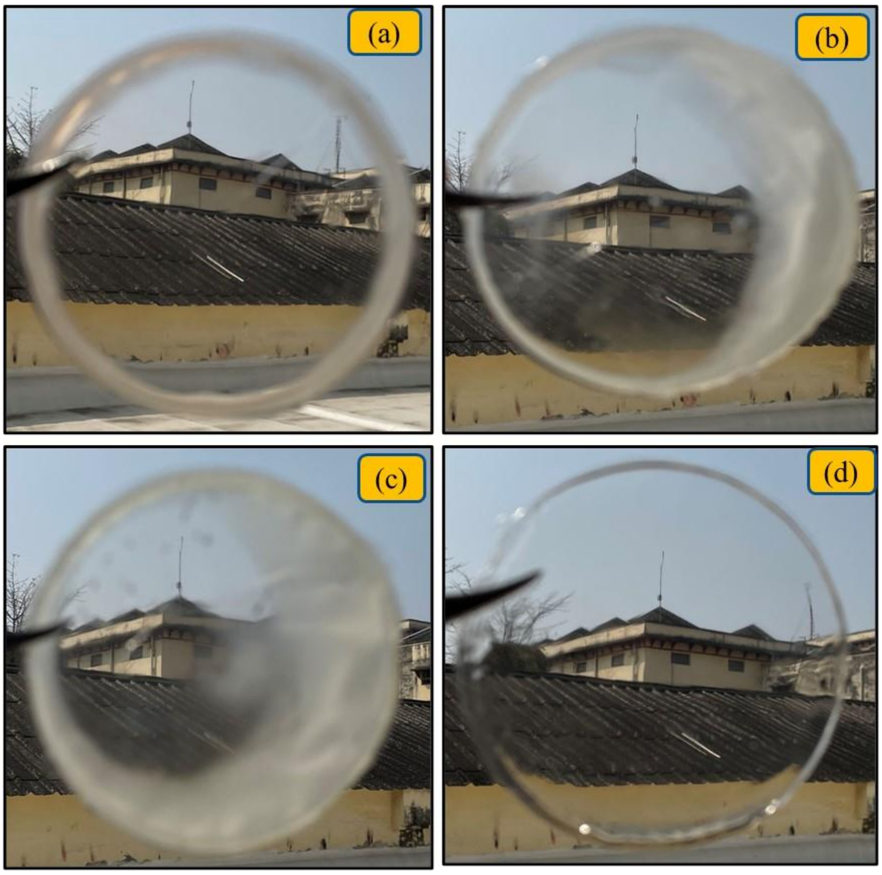

Figure 5.1-Images of the PIMs at different synthesizing temperature (a) 23 °C or less. (b, c) ≤ 21 °C (d) between 25-30 °C (Successful trials)

Figure 5.2-Effect of entrapped water droplets/moisture (through glassware/petri dish or atmosphere) on membrane

5.2 ACORGA M5640 based PIMs

After identifying the abovementioned challenges, PIMs with different composition have been prepared under optimized working condition by using two components; PVC and ACORGA M5640. The blank PVC membrane was rigid and brittle. However, as the part of ACORGA M5640 was increased, it became flexible with sufficient strength. The PIMs with maximum of 50% of ACORGA M5640 were appeared as homogeneous and transparent. The average thickness of such PIMs was measured as 45±5 µm.

5.2.1 FTIR analysis

Fingerprint and functional group regions are two main sub-parts of the infrared spectrum of any compound. In the first region, C-X (where X is chloride, fluoride, bromide, and iodide), C-C, C-O and C-N vibrations are observed with wavenumber lower than 1100 cm^{-1}. Generally, each compound produces its sole fingerprint region. Hence, it is very complicated to assign the spectra in the first region. Therefore, the second region having wavenumber more than 1200 cm^{-1} were used to understand FTIR spectrum. In our work, the IR spectra observed for the pure PVC membrane and ACORGA M5640 were same as reported in the various articles related to PVC films and ACORGA M5640 (Chen et al., 2018; Fatehi et al., 2018).

In the Pure PVC membrane spectrum (Figure-5.3a), the bands at 2968 to 2913 cm^{-1} linked to the stretching modes of the C−H bonds. Some of the characteristic peaks, showing the -CH_2 deformation (angular) modes, can be observed at 1426 and 1334 cm^{-1}. The presence of peak at 1251 cm^{-1} is due to CH_2-Cl (CH_2 Wagging). C-H wagging modes (trans and sis) can be observed at 958 and 607 cm^{-1}. C-Cl bond stretching mode are also seen at 834 and 692 cm^{-1}.

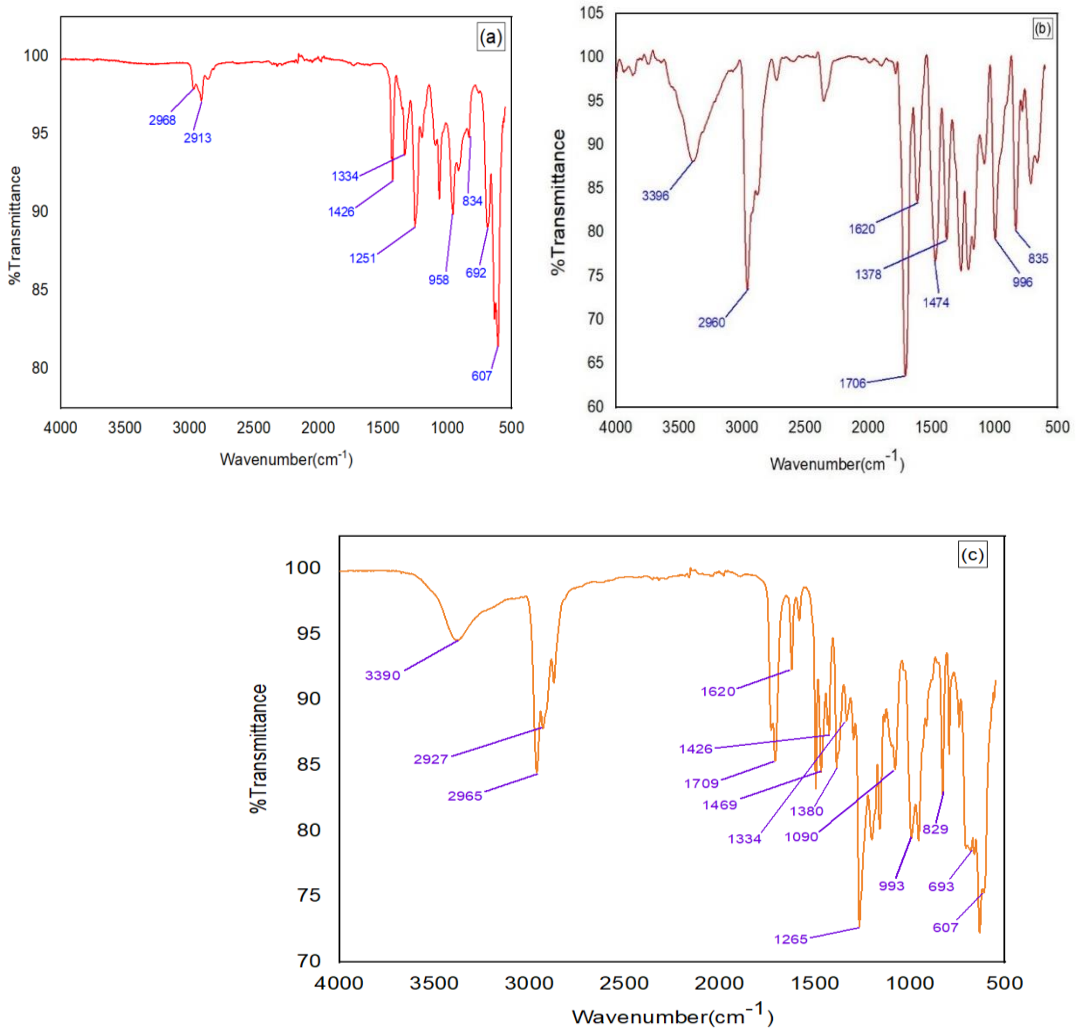

Figure 5.3-The Infrared Spectrum of blank PVC membrane (a), pure ACORGA M 5640 (b) and 50-50% PVC/ACORGA PIM (c)

The FTIR spectra of pure ACORGA M5640 (Figure-5.3b) features the existence of the characteristics group of ACORGA M5640. This spectrum shows an OH stretching vibration with a broad peak in the 3000–3600 cm^{-1} region. O-H bands from phenolic and oxime hydroxyl are centered at 3396 cm^{-1}. C–H band in nonyl and oxime are also responsible for the broad peak in the region of 3000-3600 cm^{-1}. Many other peaks at 2870-2960 cm^{-1} can be allocated to the aromatic and alkyl C-H bond stretch. The presence of sharp peak at 1700-1750 cm^{-1} shows the C=C stretching band of oxime group. The vibration band at 1474 cm^{-1} should be due to the C=C (bond stretch) in the aromatic ring of ACORGA M5640. One of the characteristic peaks at 835 cm^{-1} is resulted due to the existence of N-O single bond.

The FTIR spectrum (Figure-5.3c) of 50-50% PVC/ACORGA M5640 shows the bands of individual components of the PIM. Therefore, the bands located at 2927, 2965, 1426, 1334,1265, 829, 693 and 607 cm^{-1} could be observed in the spectra of PVC (Figure-5.3a), and the bands at 3390, 1709, 1620, 1469, 1380, 993 and 829 cm^{-1} are ascribed to the ACORGA M5640 occurrence (*figure-5.3b*). The overlapping of some characteristic bands of both the components was also observed at some bands such as at 2965, 1709, 1620,1426,693,607 cm^{-1}. Therefore, the functional groups of the both components are present also in the 50-50% PVC/ACORGA M5640 PIM. These observations recommend that chemical interactions do not occur among components throughout the membrane synthesis and there were no signs of the covalent bond formation between the polymer, and the carrier. This result is consistent with the previous reports on FTIR of PIMs (Cristina Veronica I Gherasim et al., 2011; Qiu et al., 2019; Wang et al., 2021). Thus, it is concluded that the carrier ACORGA M5640 is distributed in physical form within the long chain polymer matrix. The mechanical stability of the PIM is achieved either by Vander Waals or hydrogen bonds; weak physical interactions.

5.2.2 AFM analysis

The morphologies of blank PVC membrane and PIMs with two ACORGA M5640 contents were studied by AFM to gather information regarding the roughness profile, uniformity, and pores of membranes. 2D and 3D topographic images of these membranes (5 μm x 5 μm format) are shown in figure-5.4. The AFM observations suggested that the pores are visible in blank PVC membrane. However, the number of pores is decreasing as increasing the amount of carrier. The possible reason behind the low numbers of visible pores in PIMs could be the filling of pores by the carrier. The non-porous or dense structure of PIMs may contribute towards the enhanced chemical stability of the membrane. The 2D parameters for characterizing surface profile of membranes have been shown in table-5.1. The roughness of PIMs decreases pointedly with the increase of ACORGA M5640. The roughness values are reduced almost 80% after the addition of 50% ACORGA M5640 in the membrane and the surface seems to be relatively softer. The softer surface of PIMs was occurred due to the higher content of ACORGA M5640 in PIMs and this could be one of the possible reasons behind decrement in roughness values. The decrease in the roughness values also suggests the more homogenous surface of PIMs.

Table 5.1-Surface Roughness of studied ACORGA M5640 based PIMs (Sampling Length - 3.531μm)

Membrane Details	Roughness Average (Ra) (nm)	Root mean square Roughness (Rq) (nm)
PVC Blank Film	2.662	3.624
70%PVC/30%ACORGA M5640	0.693	0.846
50%PVC/50%ACORGA M5640	0.537	0.751

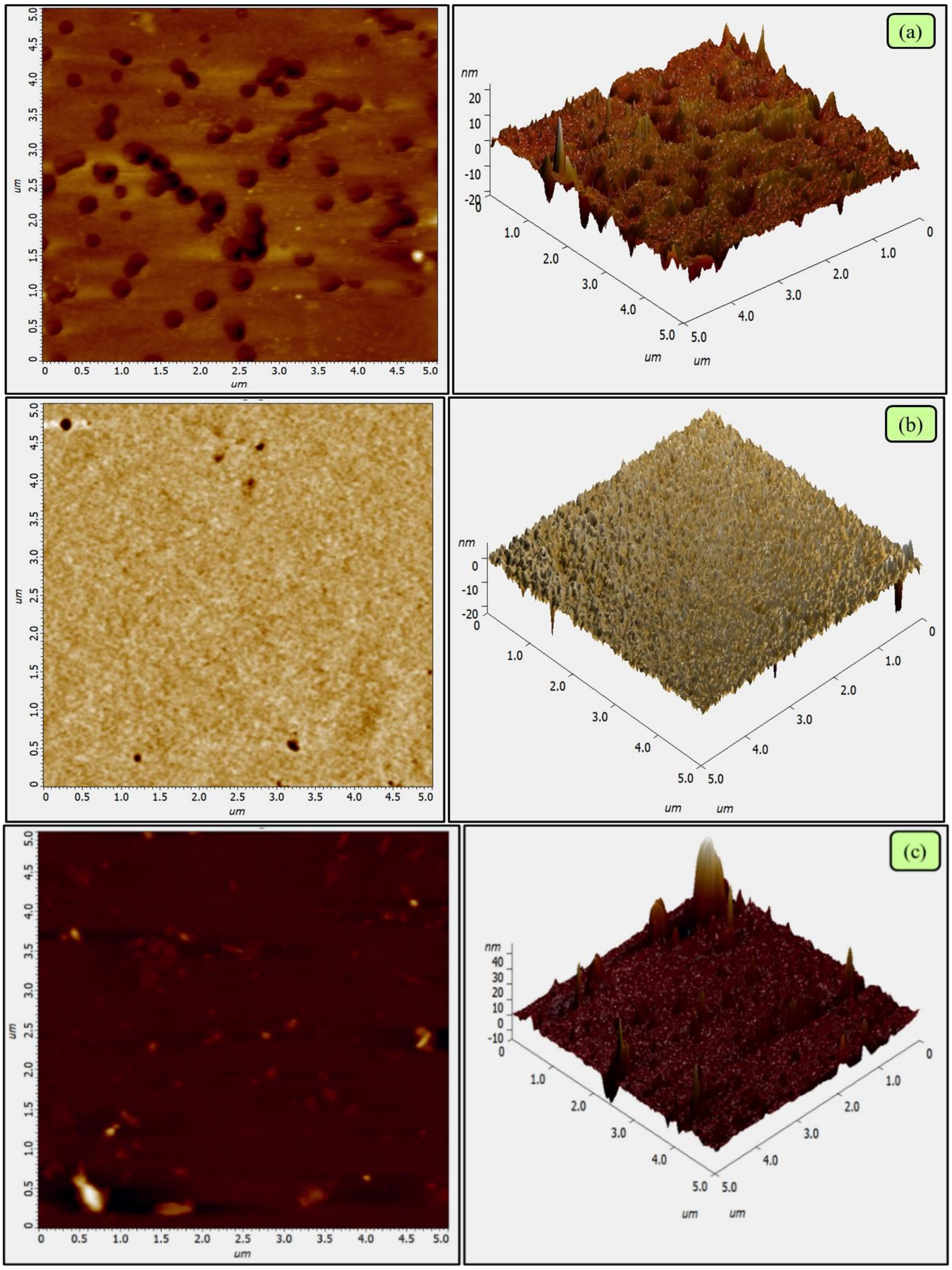

Figure 5.4- 2D (left) and 3D (right)-Atomic force microscopy (AFM) images of *blank PVC membrane (a), 70-30% PVC/ACORGA M5640 PIM (b) and 50-50% PVC/ACORGA M5640 PIM (c)*

5.2.3 Thermogravimetric analysis

Thermogravimetric analysis was done in order to know the thermal stability of the synthesized PIMs. TGA study also suggests the chemical demolition of PVC matrix within PIMs. Hence, one can have idea about maximum working temperature of PIMs. *Figure-5.5* shows thermograms of blank PVC, 70-30% PVC/ACORGA M5640 and 50-50% PVC/ACORGA M5640 membranes. The degradation of the PVC membrane arose in three stages. First degradation occurred at a temperature range 300-360 °C (65% of initial mass), which signifies the major thermal degradation of the polyvinyl chloride chains. In the second stage (350-450 °C) shows the formation of aromatic and some other compounds. Finally, in third stage, next degradation encountered at a temperature close to 450 °C (90% of initial mass). Above 520 °C, total carbonizing of the membranes occurs. The decomposition of membrane containing ACORGA M5640 can also be divided in three stages. The major mass loss begins from 180°C and occurred in temperature range 180-290 °C. This degradation is dependent of ACORGA M5640 because increment in carrier concentration also increases the rate of mass loss at this temperature. The thermal breakdown of PVC was shifted to lower temperature range in the existence carrier and this result is consistence with previous reports of PIMs research (Ocampo et al., 2009). This restricts the upper limit of carrier used in PIMs components. The second stage is shifted at lower temperature in comparison to the blank PVC membrane and it starts from 290 °C. The third stage starts above 440 °C and 90% of initial mass was lost at this level. Therefore, it can be said that adding the carrier as membrane components shows significantly decrease in the thermal stability of membrane. TGA reports suggests that the thermal stability of PIM with ACORGA M5640 is good enough to withstand its working temperature.

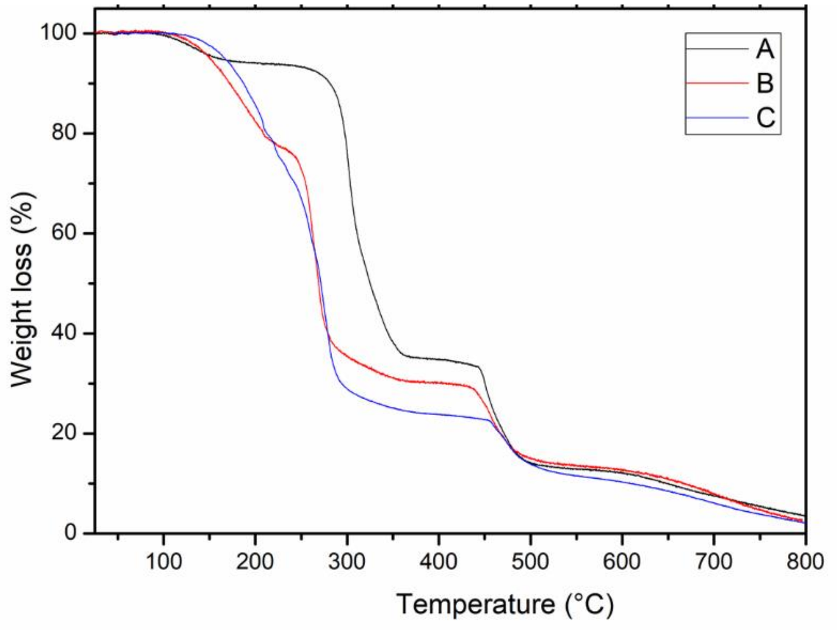

Figure 5.5-*Thermograms of blank PVC membrane (A), 70-30% PVC/ACORGA M5640 (B), 50-50% PVC/ACORGA M5640 (C)*

5.3 TBAN based PIMs

PIMs with different ratio of components (CTA and TBAN) have been synthesised at laboratory scale under previously optimized parameters. The membrane without carrier; TBAN was brittle and rigid in nature. However, introduction of carrier into membrane phase leads to increase the flexibility and softness of membrane. The PIMs with maximum of 50% of TBAN were appear as homogeneous and transparent and flexible (shown in figure-5.6) to be used for further experiments. The average thickness of such PIMs was measured as 48±5 µm.

Figure 5.6-Image of the CTA-TBAN based PIMs

5.3.1 FTIR analysis

In the IR spectra of blank CTA membrane (figure-5.7a), the broad peak in range 3502-3380 cm^{-1} has been observed due the existence of O-H bond. The less intense bands at 2970 cm^{-1} and 2870 cm^{-1} is attributed to C-H bonds. Moreover, the absorption band located at 1743 cm^{-1} is confirming the presence of stretching vibrations of the carbonyl group. The bands at 1629 cm^{-1} is corresponding to nitrate. The stretching modes of C-O single bonds have been designated at band 1246 cm^{-1} and 1054 cm^{-1}. The band at 600 cm^{-1} is representing the C-Cl bond of chloroform.

The IR spectra of pure TBAN (figure-5.7b) show some low intense peaks at 2952 cm^{-1} and 2881 cm^{-1}, which correspond to C-H bond. The high intensity peaks at 1490 cm^{-1} and 1335 cm^{-1} is linked to the nitrate group. Few lower intensity peaks were identified at 1175 and 1020 cm^{-1} due to the existence of C-N bond. Peak correspond to N-H bond are visible in the range of 870-751 cm^{-1}.

Figure-5.7c shows the IR spectra of 50-50% CTA/TBAN containing the bands of individual components (carrier and base polymer) of the PIM. Consequently, the bands located at 3499, 1740, 1370, 1231, 1249, and 600 cm^{-1} could be observed in the spectra of pure CTA blank membrane (figure-5.7a), and the bands at 1342, 1175, and 875 cm^{-1} are ascribed to the TBAN occurrence (figure-5.7b). The IR spectra of 50-50% CTA/TBAN also shows some overlapping of characteristic bands such as 2970, 2868 cm^{-1} of both the components.

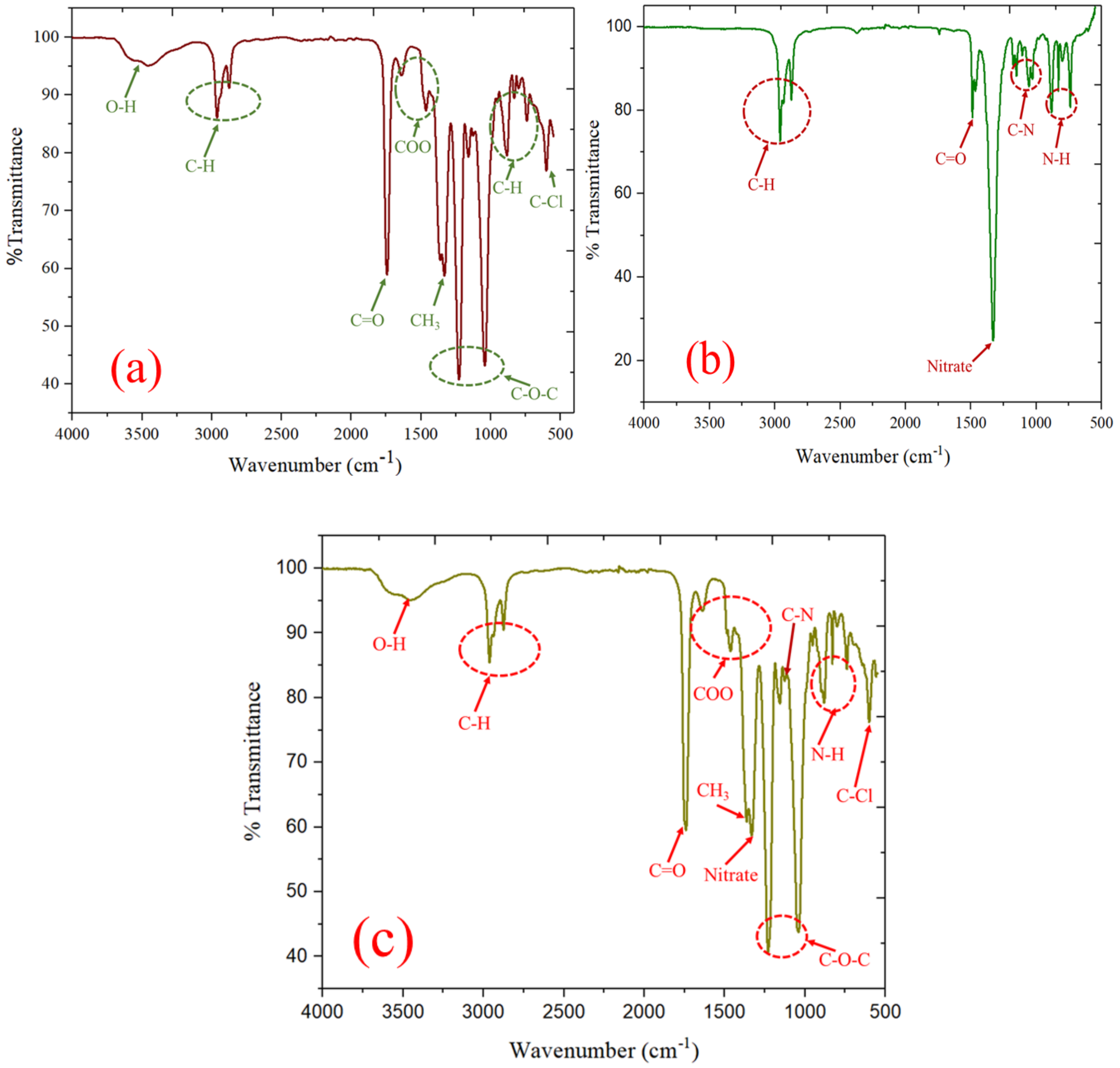

Figure 5.7-The Infrared Spectrum of blank CTA membrane (a), pure TBAN (b) and 50-50% CTA/TBAN PIMs (c)

The FTIR observation confirms the existence of functional group of both the components in 50-50% CTA/TBAN. Moreover, no new bands observed in mixed components. Therefore, FTIR spectra of individual and mixed components suggest that no chemical reaction took place during the PIMs synthesis and there was no indication of covalent bond formation observed. Further, it can be concluded that mechanical stability of PIMs is achieved by weak physical interactions as reported in our ACORGA M5640 PIMs.

5.3.2 AFM analysis

The morphologies, presence of pores, surface roughness and uniformity of blank CTA membrane and PIMs with different composition (30%TBAN and 50% TBAN) have been observed by the AFM. Figure-5.8 shows the 2D and 3D topographic images of prepared blank membrane and PIMs (5 µm x 5 µm format). There were no pores observed in the blank CTA film. Moreover, the membrane containing TBAN also doesn't contain any pores. The membrane was dense and non-porous, which basically contributes in enhancing the chemical and mechanical stability of the synthesised PIMs. Moreover, 2D parameters for characterizing surface profile of membranes for were also recorded and reported in table-5.2. The highest value of roughness was observed in blank CTA membrane. The decrease in roughness values were seen after introducing the carrier; TBAN. Moreover, the increasing carrier percentage in membrane phase decreases the roughness values. The decrease in roughness value makes the membrane more homogenous and flexible, which is beneficial for using PIMs during the transport studies.

Table 5.2-Surface Roughness of studied TBAN based PIMs (Sampling Length -3.531µm)

Membrane Details	**Roughness Average (Ra) (nm)**	**Root mean square Roughness (Rq) (nm)**
CTA Blank Film	8.522	16.678
70%CTA/30%TBAN	2.519	3.254
50%PVC/50%TBAN	2.022	2.569

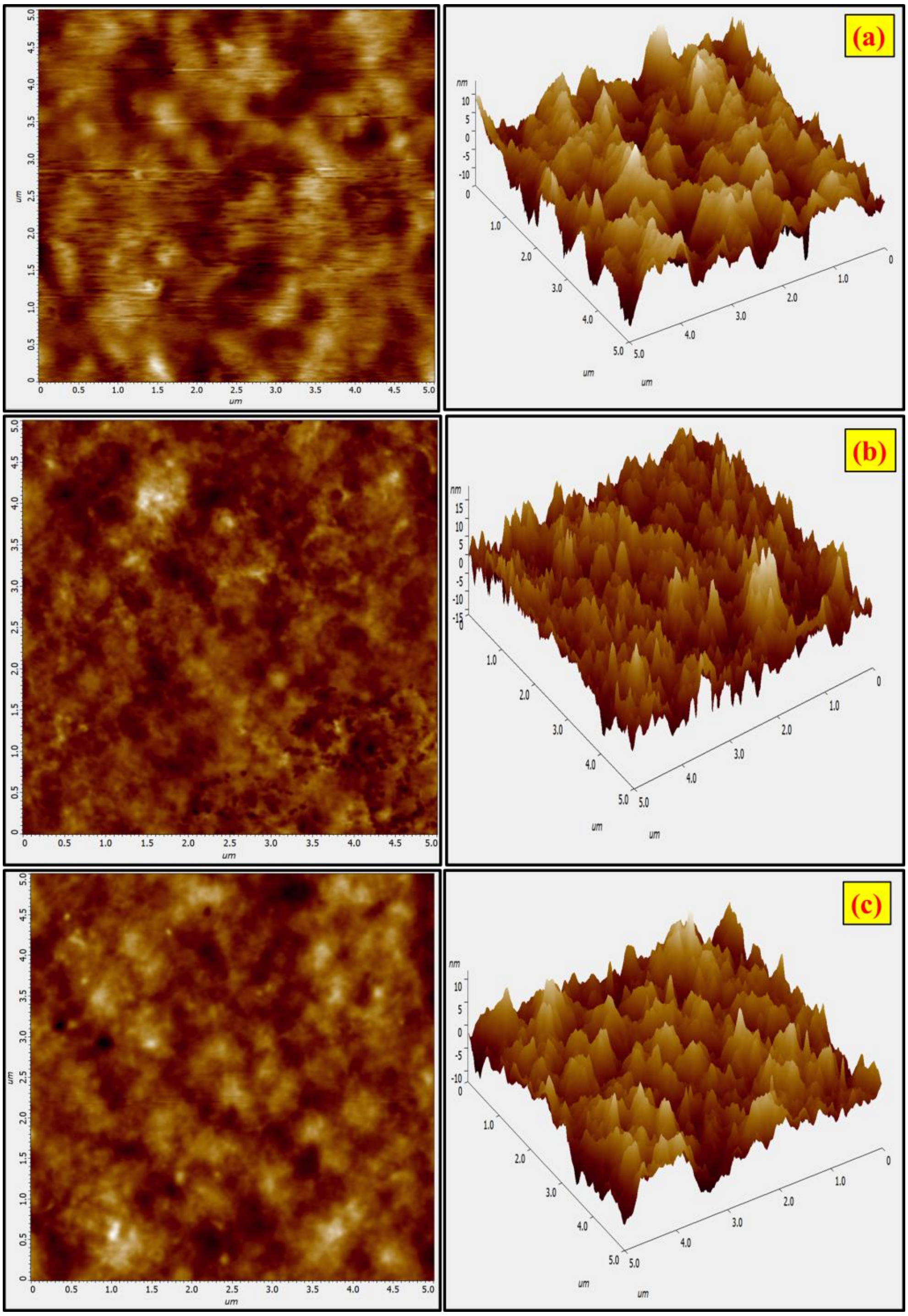

Figure 5.8- 2D (left) and 3D (right)-Atomic force microscopy (AFM) images of *blank PVC membrane (a), 70-30% PVC/ACORGA M5640 PIM (b) and 50-50% PVC/ACORGA M5640 PIM (c)*

5.3.3 Thermogravimetric analysis

The thermal stability of synthesized blank CTA membrane and PIMs were studied through TGA (figure-5.9). The degradation of blank CTA membrane occurred in mainly three stages. In the first stage, volatilization of the volatile matter or evaporation of moisture took place from 315- 29 °C. The prominent thermal degradation of CTA polymeric chains is represented by second stage (315-410 °C). Moreover, the final stage starts after 410 °C, representing the carbonization of the products to ash. The decomposition of TBAN based PIMs have also been occurred into three stages. The introduction of carrier phase into membrane increases the % weight loss into the first and second stages. It was observed that about 37.75%, 60.813% weight loss occurred in the first stage with 30% and 50% carrier. Similarly, in second stage, 48.16 %, 28.69% weight loss for 30% and 50% carrier was observed respectively. Moreover, there was slight reduction in thermal breakdown of CTA chains has also occurred after adding the carrier phase into the blank CTA membrane. TGA reports also suggested that the thermal stability of PIMs with adding more carrier content may also decrease their thermal stability.

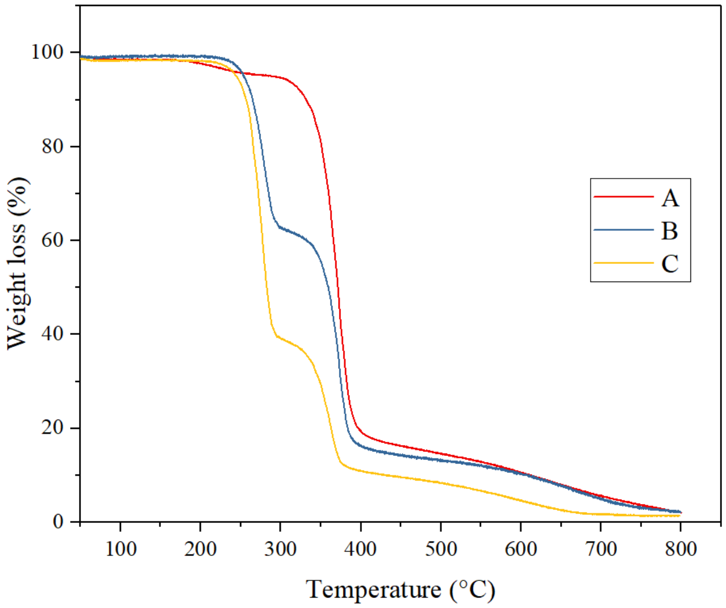

Figure 5.9- Thermograms of blank CTA membrane (A), 70-30% CTA/TBAN (B), 50-50% CTA/TBAN (C)

Conclusions

- Based on challenges faced during the current work of membrane preparation, it is observed that working temperature and use of undried glass wares may contribute to non-uniform thickness, uneven surface, and loss of transparency.
- The characterization by SEM and FTIR reveals that the polymer matrix works as a sink for the carrier to be dispersed in physical form.
- AFM results explain that the pores are filled by the carrier and the surface roughness values diminution with the increase of carrier concentration and this suggests that the prepared PIMs are homogenous.
- The newly developed non-plasticized PIMs were found to be thin, flexible, transparent, and homogenous.
- The membrane cost is coming down due to the absence of any plasticizers in the PIM composition.
- The reduction in the cost of the membrane reduces the overall cost of the membrane processes used for metal mining from the multi-metallic solutions.