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Photo-oxidative degradation of polybenzimidazole derivative membrane

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ABSTRACT

High temperature polymer electrolyte membrane fuel cells (HTPEMFCs) are energy efficient systems with the potential to address all energy issues of present and future generations. Polybenzimidazole (PBI) based high temperature fuel cells are subject of high importance because PBI membranes are proved to be one of the best candidates for high temperature fuel cell applications. The stability of PBI membranes has been identified as crucial issue for the long-term durability under oxidative conditions of fuel cells. The present investigation highlights the photo-oxidative degradation studies accomplished on polybenzimidazole based poly(2,2'-butylene-5,5'-bibenzimidazole) (PBIB) membranes. The PBIB polymer membranes are found suitable for both in high temperature fuel cells as well as other high temperature applications. In this research article, PBIB membranes were photoirradiated under polychromatic UV rays ($\lambda > 290$ nm). The photo-oxidative degradation of membranes was characterized by Fourier transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). FT-IR results showed significant amount of photo-oxidation and chemical degradation in fuel cell membranes which is proposed to be initiated by free radical mechanism. SEM images revealed development of nano-dimensional cracks and holes on surface of membranes which indicate structural and morphological degradation. The present study showed better results of accelerated photo-degradation as compared to the oxidative degradation results already reported in literature obtained chemically and thermally. Hence, the proposed photo-oxidative degradation method may be useful in determining stability, life time expectancy and degradation mechanism of fuel cell and other high performance membranes. Copyright©2013 VBRI press.

Keywords: Degradation; fuel cell; membranes; photodegradation; polybenzimidazole; UV irradiation.

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Introduction

The energy and environment are the thrust area of research and need of the human society all over the world **[1]**. Now-a-days more emphasis is given to the eco-friendly and green processes of energy production to save this planet from various kinds of pollutions (specially like air, water, soil, radiation, etc.) for its sustainability **[2, 3]**. Naming a few eco-friendly energy systems like, solar energy, wind energy, tidal energy and fuel cell energy are the important green processes of energy production **[4, 5]**. Amongst them fuel cells and solar cells are looked upon as the most feasible and sustainable technology of the future to fulfill mass energy requirements **[6, 7]**. In this paper we are focusing on fuel cells and more specifically on the stability of polymer electrolyte membranes. The fuel cell performance for longer hours is very important for their successful implementation in automobile industry. The stability of membranes is affected by the oxidizing environment of the fuel cells **[8, 9]**. The various factors like temperature, humidity and acidity also contribute to the membrane failure **[10]**. It has been found that fuel cell conditions are favorable for the generation of free radicals.

Fuel cells are based on a principle of electron transport across polyelectrolyte membranes (PEM's) which are made up of high performance polymers. In the present investigation emphasis is given to the polybenzimidazole derived engineered polymer membranes having rigid and flexible backbone structures for degradation study. Acid doped PBI membranes are attractive as electrolytes in high temperature fuel cells **[10-13]**. The chemical structures of PBI and PBIB are represented in **Fig. 1**. Some literature is available on the chemical and thermal degradation study of PBI membranes with fuel cells perspectives but, the photo degradation study on the same is not yet reported **[8-10, 14-20]**.

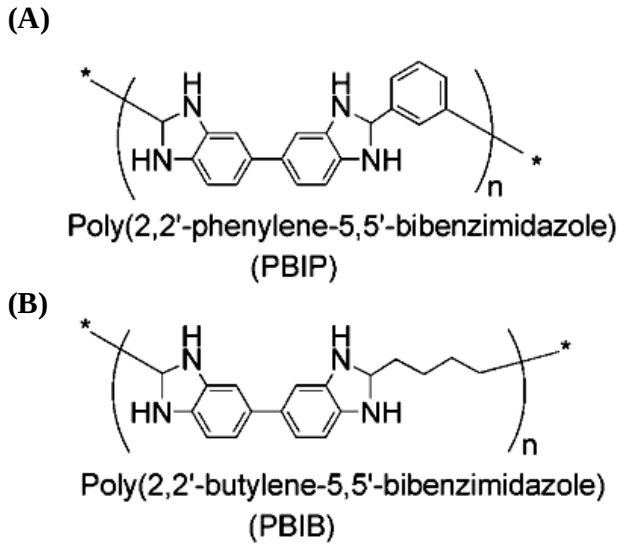

Fig. 1. Chemical structure of Polybenzimidazole polymers; (A) PBIP and (B) PBIB.

There are several articles which emphasized on membrane stability and related it to the fuel cell performance **[8-10, 15-19, 21]**. The thermal degradation work extensively studied by the Musto et al. revealed that it is the oxidation of the PBI membranes which leads to their degradation **[22]**. Later on it was found that the membrane oxidative-degradation affects the chain length and the chemical nature of the PBI **[23]**.

It has been proved by the Panchenko et al. and other groups that membrane degradation takes place due to generation of hydroxy and peroxy radicals in the fuel cell conditions with the active role of Pt catalyst **[24]**. The other experiments however reported that the main membrane degradation occurs due to the loss of acid groups from the polymer chain **[25-27]**. Experimentally, to generate peroxide radicals various methods have been adopted by previous researchers by chemical means. For this, the most efficient Fenton reagent is used which is composed of H_2O_2 and Ferrous salt. The reaction of Fe^{2+} with H_2O_2 generates hydroxy and peroxy radicals. The Fenton degradation method has been frequently used to determine the fuel cell membrane stability and weight loss **[1, 9-11, 13, 16, 19, 23, 28-30]**. Some groups reported no change in chemical and physical properties of membranes but some groups like Chang et al. reported the change in molecular weight and tensile strength after Fenton treatment of the membrane **[10, 21, 31]**. The Fenton studies revealed that chemical changes take place between 4000 cm^{-1} and 2800 cm^{-1} which basically resemble to the N-H and C-H stretching modes of benzimidazole rings. The PBI membranes absorb moisture if exposed to air which is reflected by their FT-IR spectrum having broad peak in the region between 4000 cm^{-1} and 2400 cm^{-1}. The more significant results are reported in the region between 1000 cm^{-1} and 1900 cm^{-1} in the FT-IR spectrum which reveals to the formation of many oxidized carbonyl products **[23]**. The thorough study of these products by the mass spectroscopy may reveal significant results which may further be helpful in determining the correct mechanism of degradation. The oxidative degradation leads to many physico-chemical changes in the polymers. These changes can be very well understood by the thermal and chemical analytical techniques.

The present work also reports oxidative degradation of fuel cell membranes under the radical attack but, here the radicals are generated by photo-thermal process. The UV radiations have enough energy which may lead to bond scissions via free radical generation. The UV degradation and the lifetime expectancy of many commercially available polymers have been extensively reported in the literature **[32-34]**. The effect of fillers and nanomaterials on the degradation and stabilization of many polymers is evaluated by UV irradiation process. Thus, by photodegradation study we may find out the mechanism of degradation on one hand and the fast/accelerated degradation of the desired polymer on the other **[35]**. We have assumed that the oxidative degradation of the polymer membranes in the fuel cells environment will resemble to those generated in the UV irradiation chamber.

This study is unique and novel as it is the first photo-oxidative degradation study on PBIB polymer applicable in fuel cells. There is only one report about photodegradation on PBI polymer accomplished by George et al. but with different approach and objectives. They have carried out the photodegradation study on PBI by UV irradiation process and characterized the degraded polymers by

Ultraviolet spectroscopy which revealed the absorption shifts towards higher wavelength. Here, we are giving a more detailed study of PBIB degradation with a clear objective of their application in high temperature fuel cells and other high temperature applications **[14]**. This investigation gives accelerated mode of degradation study on such high performance aromatic polymer materials. The uniqueness of this work is the repeatability of results and the faster characterization of PBI membranes as compared to thermal degradation and Fenton's tests. Efforts are made to compare the results found in present investigation with those which are reported in literature being performed either by thermal or chemical degradation modes. The present photo-oxidative accelerated degradation method may prove useful in determining stability, life time expectancy and degradation mechanism of high performance polymer membranes.

Experimental

Materials

3, 3'-Diaminobenzidine (DAB ≥ 99 %, Sigma Aldrich, USA), Adipic acid (AA ≥ 99 %, Fluka, India), Polyphosphoric acid (PPA ≥ 84 %, Merck, India) and Formic Acid (FA ≥ 98 %, Baker, India) were used for the synthesis of PBIB polymer and membrane casting.

PBIB synthesis

The PBIB polymer was synthesized by following the scheme as summarized by Bhavsar et al. **[14]** and shown in **Fig 2**. The PBIB polymer was obtained by the polycondensation method using three necked round bottle flask to ensure inert atmosphere (N_2 supply), constant stirring and calcium chloride trap for absorbing reaction moisture. DAB added and stirred with the excess amount of hot PPA followed by addition of equimolar amount of AA. The reaction was performed first at elevated temperature of 180 °C four 5 hrs, further at 200 °C for 8 hrs. The obtained highly viscous solution of PBIB was further purified by several washings with deionized water and treatment with basic media to remove excess of acid. The PBIB polymer was dissolved in formic acid and the resultant solution (5% w/v) was vacuum dried in different volumes in two different membrane casting plates for 3 days at 100 °C. The thickness of the casted membranes was measured 40 µm and 75 µm.

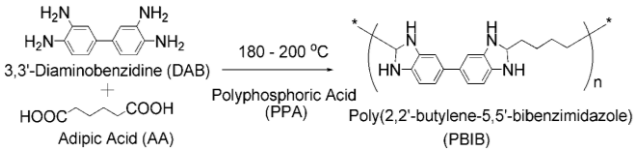

Fig. 2. Schematic representation of synthesis of PBIB polymer **[14]**.

Sample preparation

The samples of PBIB were prepared by cutting polymer films in the dimensions of 2 cm × 1 cm for oxidative photo-degradation studies. The PBIB samples were photo-irradiated under polychromatic UV rays for 100 hours by using the SEPAP 12/24 instrument, France as described in **Fig. 3**. The photo-oxidized membranes were characterized before and after the irradiation process to find the effect of polychromatic UV rays in chemical degradation.

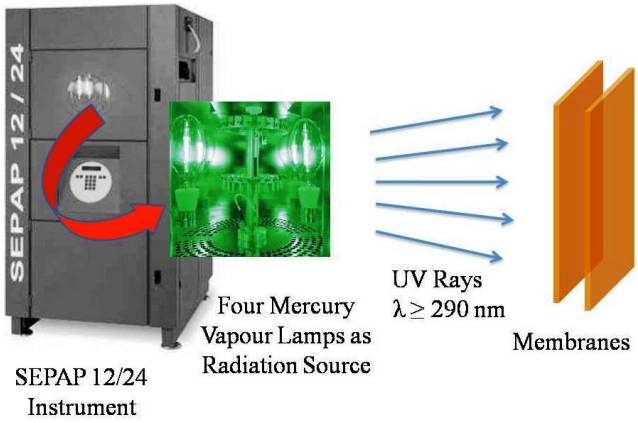

Fig. 3. Schematic representation of the UV-irradiation process of membranes. (SEPAP 12/24 instrument and Vapour lamps are reproduced with permission. Courtesy of Atlas Material Testing Technology GmbH, Germany).

UV-irradiation of PBIB samples

The photo-oxidative degradation studies on PBIB polymer were carried out by irradiating PBIB samples under polychromatic UV-rays with the wavelength (λ) ≥ 290 nm. The Pyrex filter was used as an envelope to ensure λ ≥ 290 nm in SEPAP 12/24 Instrument (manufactured by Materiel Physico Chemique, Neuilly, France). The UV irradiation chamber of this instrument consists of four 400 W low pressure mercury vapour lamps. The average distance between the samples and the glass was measured to be about 15 cm. A constant temperature of 55 °C and filtered air supply was maintained throughout photo-irradiation process to facilitate accelerated degradation/oxidation of membranes.

Materials characterization

The photo-oxidative degradation studies were accomplished by characterization of polymer samples under Fourier transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). The samples were characterized before and after the photo-irradiation of the samples for comparative study.

FT-IR spectroscopy

The chemical aspects of membrane degradation were studied by FT-IR spectroscopy. The polymer samples were studied under ATR mode (using a diamond prism) in GX Perkin Elmer FTIR instrument for UV degradation study. The polymer samples were given 16 scans each at a resolution of 4 cm^{-1} in the range of 4000 to 600 cm^{-1}. All the membrane samples were directly scanned after irradiation in ATR mode without any sample preparation. The obtained spectra were plotted after ATR correction.

Scanning electron microscopy

To study the effect of UV irradiation on surface and morphology of PBIB membranes, SEM study was done.

The polymer samples were scanned on SEM (Leica Stereoscan 440) operated at an accelerating voltage of 20 kV. The pre-scanned samples were sputter coated with 10 nm thick layers of gold nanoparticles by using a Polaron SC 6420 sputter coater. The neat and irradiated samples were sputter coated without any pre-treatment or sample preparation.

Results and discussion

The chemical changes of polymer degradation were characterized by FT-IR spectroscopy. The neat membranes were analyzed under FT-IR which showed the non-existence of any peak in the region between 1800 cm^{-1} to 1660 cm^{-1}. **Fig. 4** shows FT-IR spectrum of PBIB polymer observed before and after 100 h of polychromatic UV irradiation. The advantage of the present study is that all the photo-irradiated samples were scanned in ATR-mode without any pre-treatment or sample preparation. Here, the studied polymer samples were not subjected to contact with any chemicals or with liquid/solid reactants, hence no treatment was needed to remove any foreign material before characterization. On the other hand, in case of chemical degradation or thermal degradation processes sample preparation requires washing, overnight vacuum drying, and pellet formation which are time consuming and many chemical changes may take place during the sample preparation treatments itself. Moreover, the consistency of results will also depend upon the mode of sample preparation, which is totally avoided in the present study.

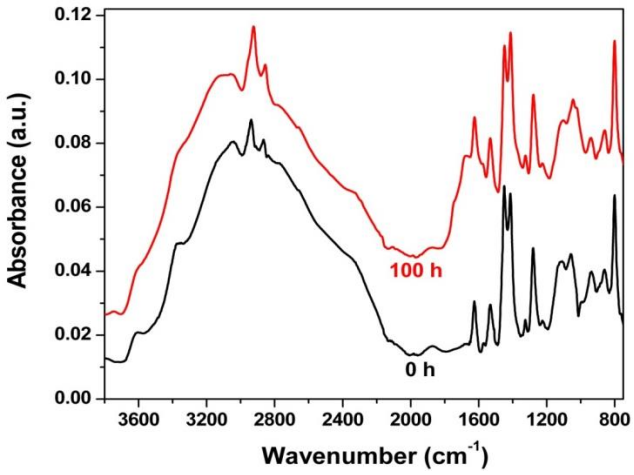

Fig. 4. The FT-IR spectrum of polybenzimidazole membranes (PBIB) before (0 h) and after (100 h) polychromatic UV-irradiation.

As a result of polychromatic UV irradiation, several significant changes were observed in carbonyl region which are clearly reflected by **Fig. 5**. A number of signals were observed which emerged in the region from 1800 cm^{-1} to 1500 cm^{-1}. An immense increase was observed in the absorption frequencies in carbonyl region from 1780 to 1650 cm^{-1} which is attributed to the formation of various photo-oxidative products as a result of UV irradiations **[35]**. The broad signal evolved after degradation shows clear peak at 1683 cm^{-1} which is attributed to the formation of C=O groups in the polymer backbone extended till 1723 cm^{-1} **[13]**. There is a peak observed at 1747 cm^{-1} which may be attributed to the formation of some aldehydes after the chain scissions **[22]**.

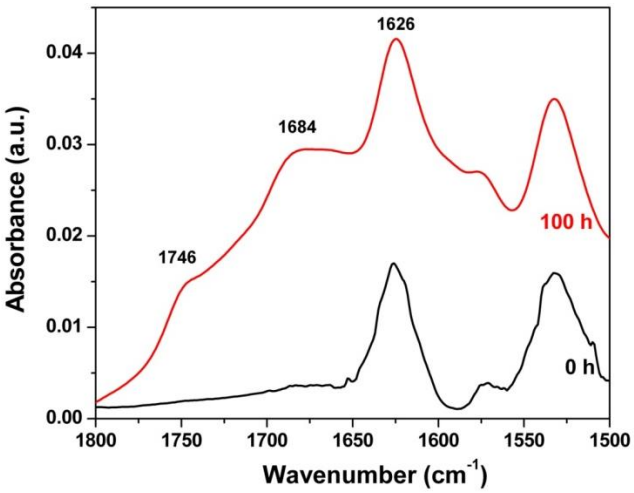

Fig. 5. The carbonyl region of PBIB membranes as recorded by FT-IR spectroscope in the range of 1500 cm^{-1} to 1800 cm^{-1}.

The growth of carbonyl content at 1715 cm^{-1} in photoirradiated polymer samples is represented in **Fig. 6** which is attributed as a result of photo-oxidative degradation caused by UV rays. This indicates the oxidation of the benzenoid and imidazole rings by the formation of C=O groups. Further, this may also be attributed to the formation of various carbonyl groups/products whose formation may led to the scission of benzimidazole rings and may further result in the decrease in the mechanical properties of membranes.

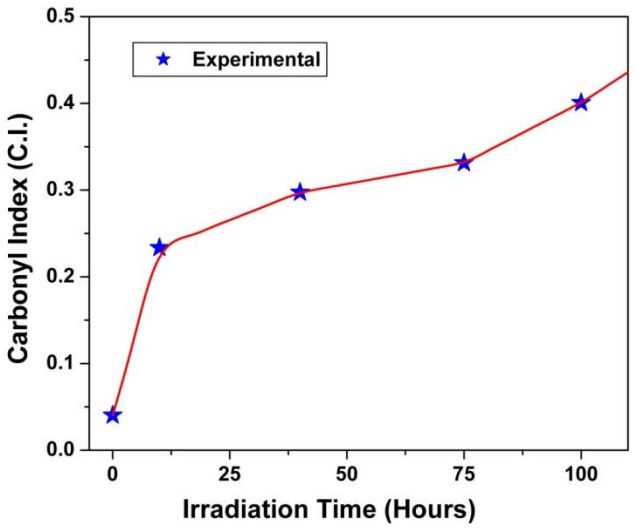

Fig. 6. The carbonyl index of PBIB membrane measured at 1715 cm^{-1} with the polychromatic UV irradiation time.

The degradation rate was observed to be more in the initial hours of irradiation as compared to the later stages of irradiation. The carbonyl index fits linearly after 10 hours of irradiation which may be attributed to the constant rate of degradation thereafter. The fast degradation process in the initial 10 hours is an indicative of high absorbance of UV rays by the aromatic parts of polymer and their further

activation in the form of free radicals. These free radicals are responsible for the fast degradation rate in initial 10 hours of photo-irradiation. The above findings may be attributed to the formation and attack of polymer radicals on molecular oxygen which further resulted in the formation of different carbonyl functionalized end products like carboxylic acid/ketones/ethers/esters etc **[36]**. The formation of these products was confirmed by the increased absorbance in the broad range of 1800 cm^{-1} – 1650 cm^{-1}, which is revealed by the FT-IR spectroscopy. The C-H stretching peaks were found to be less affected by the irradiation process as no significant change in their absorption frequency is observed. These result match with the earlier published reports of the other aromatic polymers and show stability of benzenoid ring towards radicals [13]. There are two changes observed in the region between 3000 cm^{-1} to 4000 cm^{-1}, first is the decrease in the absorbance at 3420 cm^{-1} and increase in the absorbance at 3608 cm^{-1}. The decrease in the absorbance at 3420 cm^{-1} may be attributed to the N-H bond scission of the imidazole ring which may be the point of initiation of free radical mechanism of degradation. On the other hand the increase in the absorbance at 3608 cm^{-1} indicates the increase in the –OH and -OOH groups. The hydroxyl and perhydroxyl groups are formed only as a result of free radical mechanism of degradation. The formation of these products indicates that Norrish type I and Norrish type II chain scissions takes place during oxidative degradation **[37]**. These initial findings of photo-oxidation of polybenzimidazole based polymer are also expected to be the breakthrough in surface modification of PBI membranes for increased water retention and other useful properties.

The **Fig. 7** shows the growth of hydroxyl index measured at 3608 cm^{-1} with UV irradiation time. This synergy is found between the hydroxyl index and the UV irradiation time **[38]**.

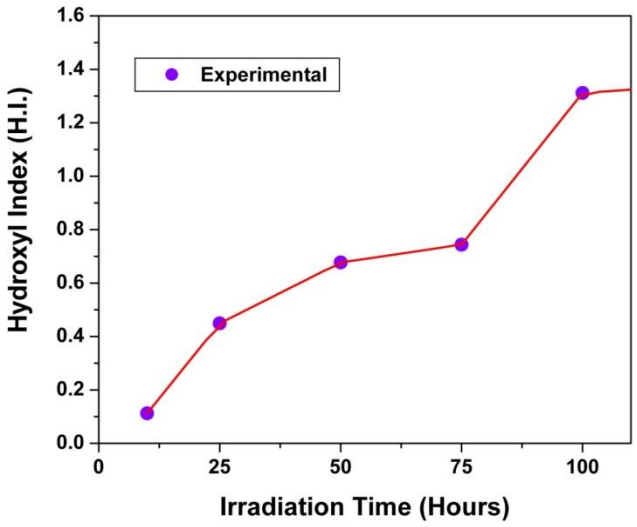

Fig. 7. The hydroxyl index of PBIB membrane calculated at 3608 cm^{-1} with the polychromatic UV irradiation dose.

Herein, a faster degradation rate was observed at initial hours of UV irradiation but found to slow down with the increase in photo-irradiation hours in range of 80 – 100 h. This may be attributed to the formation and attack of oxygen radicals or diradicals on polymer chains leading to the formation of hydroxides and peroxides **[28]**. As a result an absorbance peak at 3608 cm^{-1} was found to increase with UV dose which is reflected back in the hydroxyl index. It is also found that there is enough drift from linear fit, which indicates that degradation in the PBI based polymers takes place in disordered manner. The degradation rate was very high initially, slowed in the middle and accelerated later on.

The effect of thickness on the membrane degradation showed that the thin membranes degrade faster and show strong absorption in FT-IR spectrum as compared to the thick ones **[13]**. Similar results are found here which may be attributed to the changes taking place as a result of free radical generation and their attack on the polymer chain. The thin films show greater absorbance of radiation due to deep penetration which results in more degradation. On the other hand, the thicker films showed delayed degradation and lesser absorbance as compared to the thin membranes. This may be attributed to the fact that, deeper penetration is not possible in thick membranes and thus the effective degradation takes place at the surface only which results in lower absorbance in FT-IR.

SEM images were taken before and after the photo-irradiation to investigate the morphological changes take place on polymer surface as a consequence of photo-exposure which is shown in **Fig. 8**.

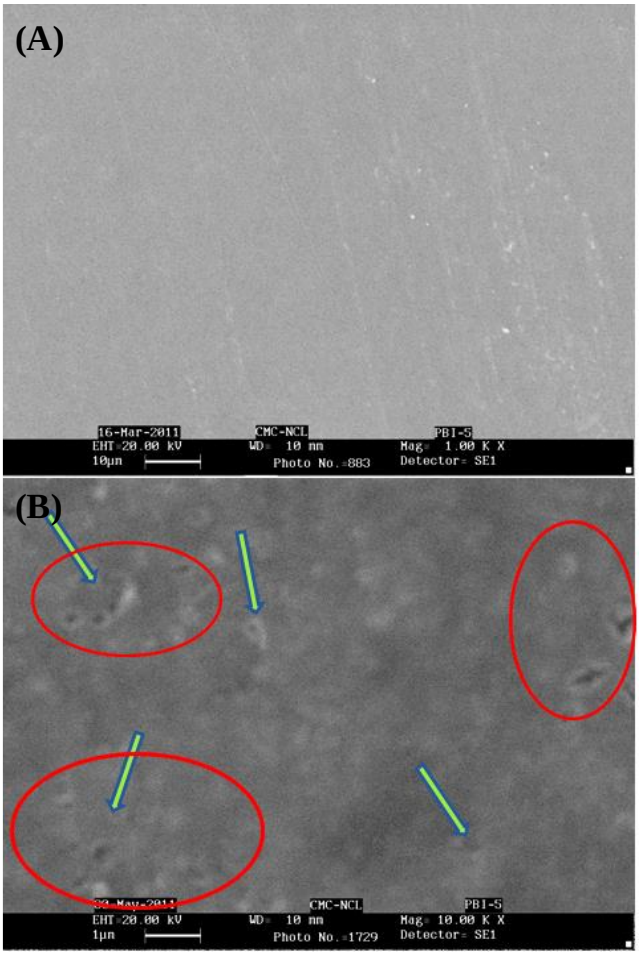

Fig. 8. SEM images of PBIB membranes captured before (A) after (B) polychromatic ultraviolet irradiation.

The figure shows smooth and uniform surface of polymer membrane before UV irradiation. The polymer membranes were directly sputter coated after photo-irradiation without any further preparation which is otherwise not possible with the other modes of degradation used for Fuel cells and other membranes. Therefore we rarely see the SEM analysis of chemically treated membranes. Literature reports the formation of dense polymer membranes by PBI with the excellent gas barrier properties **[39]**. Photoirradiated PBIB membranes show increased roughness on membrane surface along with the formation of cracks and holes which may be attributed to the occurrence of photo-oxidative degradation due to chain scissions and cross linking in PBIB polymer chain. These SEM findings are very important from the performance, efficiency and durability perspectives. It may also be attributed that the formation of nano dimensional cracks and holes will certainly result in the deterioration of all physical and mechanical properties of the membrane which may led to the failure in its performance as a polymer electrolyte membrane (PEM) **[40]**. Hence, there is an urgent requirement for detailed and comparative study of such membranes by photodegradation method to investigate the effects of prolonged hours of UV exposure on chemical nature, morphology and their mechanism of degradation to predict their lifetime expectancy.

Conclusion

The polybenzimidazole derived PBIB polymer membranes were successfully investigated for photo degradation by polychromatic UV rays under oxidative conditions. The FT-IR results revealed the mechanism of photo-oxidative degradation which was confirmed by evolution of absorption signals in the carbonyl and hydroxyl regions. The SEM results were found in accordance with the FT-IR findings and revealed the formation of nano dimensional cracks and holes on the exposed membrane surface. It may be concluded that formation of nano dimensional cracks and holes will certainly result in the deterioration of all physical and mechanical properties of the membrane which may led to failure in its performance as a polymer electrolyte membrane (PEM) as well as in other high temperature applications. The extent of degradation was found to increase with the UV irradiation dose due to chemical changes which may be the prime cause of membrane failure. These findings may also be useful in surface functionalization of such membranes which further led to the enhancement of proton conductivity with increased water retention ability. In the present study it has been also observed that the appearance and disappearance of the respective peaks after photo-degradation are very similar to those published by several groups via thermal and Fenton test. Only the difference observed is that of the absorbance intensity of the respective peaks which are more in present photo-irradiation study. Thus, we may also conclude that photo-degradation study may prove to be a landmark in the accelerated study of degradation and stability of fuel cell membranes and in their life time prediction.

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