Effect of UV rays on degradation and stability of high performance polymer membranes

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ABSTRACT

Acid doped polybenzimidazole membranes have emerged as an efficient electrolyte for high temperature polymer electrolyte membrane fuel cells (HTPEMFCs). The long term stability of polybenzimidazole membranes has been recognized as an important issue for commercial applications. Here, we report the oxidative degradation of polybenzimidazole membranes. The photoirradiation of poly(2,2'-ethylene-5,5'-bibenzimidazole) (PBIE) under accelerated photodegradation conditions was carried out by ultraviolet (UV) rays ($\lambda > 300$ nm) and characterized by Fourier transform infra red (FT-IR) spectroscopy, scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXD) and contact angle measurements (CAM). The thermal properties of PBIE membranes were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) which revealed a lowering in thermal stability after photodegradation. FT-IR spectra revealed high absorbance in the carbonyl region in photoirradiated membranes whereas SEM showed nano structures / defects on the polymer film surface. CAM results showed enhancement in hydrophilic behavior and WAXD revealed increase in amorphous nature upon irradiation. Copyright © 2014 VBRI press.

Keywords: Degradation; fuel cell; high performance material; polybenzimidazole membranes; photodegradation; UV rays.

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Introduction

Polymers are one of the most extensively and widely used materials today. Polymeric materials have gained importance because of the wide scope of chemical modifications. In the several past decades, millions of tons of advanced materials for high end applications with a potential for commercialization have been synthesized. These synthetic materials have been associated for a long time with the present global environmental issues of water pollution, retardation in soil fertility and threat to habitat of marine and aquatic animals [1-5]. To overcome some of the environmental issues, it is necessary to study the factors responsible for the reduction of performance of the materials and engineer them for better performance [6]. The study of polymer degradation and stabilization is one of the multipurpose processes by which one may modify the materials to overcome the environmental concerns regarding safe disposal and decomposition of polymers [7-9]. In polymer electrolyte membrane fuel cells (PEMFCs), acid doped polymer membranes (Nafion, PBI, etc.) are used as an electrolyte to enhance the fuel cell performance [10]. These polymer electrolyte membranes (PEMs) are used in highly humid and acidic environments at elevated temperatures [10, 11]. The reduction in fuel cell efficiency has been observed on prolonged usage which is a major hurdle in large scale commercialization. It is generally accepted that the degradation of polymer membranes is one of the probable factors for performance deterioration [12-16]. There is immense scope to investigate the factors responsible for the membrane degradation [10].

Besides fuel cell applications, because of their high thermal and mechanical strength, PBIs are used in the manufacture of protective thermal clothings, components for nuclear and aerospace industries, adhesives and composite materials [17, 18]. Due to highly dense packing and small pore size, these membranes find application in other high temperature tasks and gas separations. Degradation studies of PBI-based polymer membranes have been reported by chemical, thermal and computational methods [13-16, 19-23]. Oxidative degradation of the fuel cell membranes have emerged as a major factor responsible for performance degradation of the fuel cells [10, 24].

Degradation studies play significant role in the evaluation of performance of the polymer materials. It provides useful information about material's stability, degradation behavior, mechanism of degradation, mechanical changes which occur during the course of their application [25]. The information regarding the weak bonded linkages of the polymer chains, which are prone to degradation, could be assessed by the degradation studies. Such weak linkages may be transformed into stronger ones by chemical modifications [8]. On the other hand, accelerated degradation studies may also be used as a tool for faster disposal of materials. Photodegradation is favored among few popular methods of accelerated degradation studies. Photodegradation may be achieved by high energy γ-rays, X-rays and UV rays. Among them, γ-rays and X-rays are highly energetic and destructive in nature whereas comparatively softer UV rays are widely used for photo-degradation studies [26]. Radicals such as hydroxy radicals, peroxy radicals and the oxygen diradicals are easily generated and damage polymer chains on photoirradiation [2, 13, 25-28]. Photodegradation changes may be easily monitored by FTIR spectroscopy in the hydroxyl and carbonyl regions [21-23]. Consequent mechanical changes like tensile strength, modulus and morphological changes like development of cracks, fractures, holes have been reported for several polymers [29, 30].
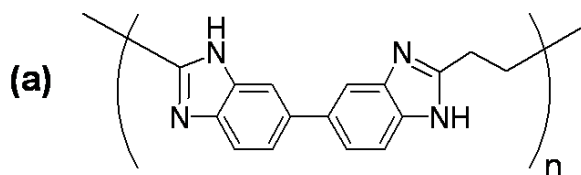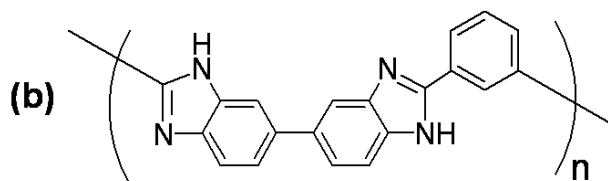
Fig. 1. Molecular structures of (a) PBIE and (b) mPBI.

In the present work, the accelerated photodegradation studies were undertaken to evaluate the stability of PBIE membrane for various high performance applications in oxidizing conditions. The structures of PBIE and conventional mPBI are shown for comparison (**Fig. 1**). The accelerated photo degradation under UV irradiation and stability of PBIE membranes are thoroughly discussed. Based on the results obtained, a mechanism of degradation is being proposed.

Experimental

Materials and methods

3,3'-Diaminobenzidine (DAB ≥ 99 %, Sigma Aldrich, USA), succinic acid (SA ≥ 99 %, Sigma Aldrich, USA), polyphosphoric acid (PPA ≥ 84 %, Merck, India) and formic acid (FA ≥ 98 %, Baker, India) were used for the synthesis and preparation of PBIE membrane [31]. Poly(2,2'-ethylene-5,5'-bibenzimidazole) (PBIE) polymer was received as gift from Membranes and Separations Group, CSIR-National Chemical Laboratory, Pune, India. PBIE was synthesized by solution polycondensation method as described by Bhavsar et al. who also report the properties significant to fuel cell applications [31]. Polymer films of 55 μm thicknesses were prepared by solution casting method using formic acid (5% w/v) solution. The polymer films obtained were vacuum dried at 80 °C for 72 hours. Samples of PBIE films (2 cm × 4 cm) were used for further studies.

For photoirradiation study, PBIE samples were clamped on a rotating vertical shaft inside the UV irradiation chamber at 55 °C in SEPAP 12/24 Instrument (manufactured by Materiel Physico Chemique, Neuilly,

France) with a constant flow of filtered air. PBIE samples were irradiated by UV radiations having wavelength above 300 nm. Four mercury vapour lamps were employed as UV source and located at four corners of the chamber lined with highly reflective aluminium coatings. Samples were irradiated for 0, 10 and 25 hours and further irradiated at regular interval of 25 hours for a total of 250 hours. The irradiated samples were taken out at regular intervals for characterization.

Characterization

Virgin and irradiated polymer films were characterized by FTIR, XRD, DSC, TGA, SEM, and contact angle measurements. Samples were scanned by attenuated total reflectance (ATR) in absorbance mode using GX Perkin Elmer FT-IR instrument to investigate the chemical changes that occurred due to UV-rays. Each sample was given 32 scans at a resolution of 4 cm^{-1} in the range of 4000 cm^{-1} to 600 cm^{-1}. Each spectrum was ATR corrected using Perkin Elmer system software before plotting. Inherent viscosities (η_{inh}) were measured at a polybenzimidazole concentration of 0.2 g dL^{-1} in 98% H_2SO_4 at 35 ± 0.1 $^{\circ}$C using an Ubbelohde suspended level viscometer.
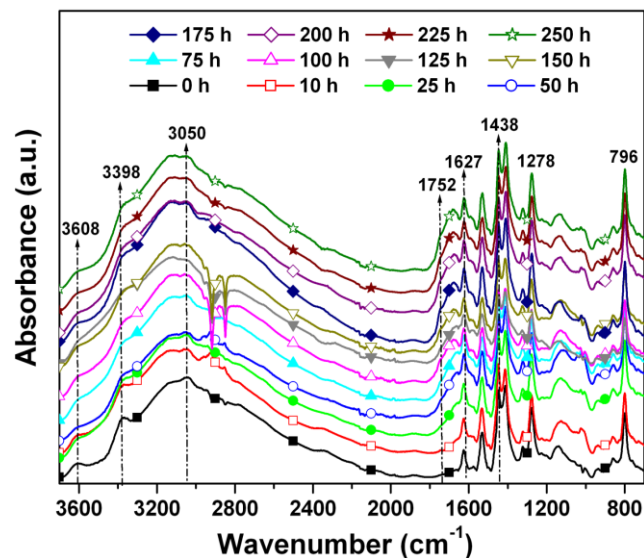

Fig. 2. FTIR spectra of UV irradiated poly (2, 2'- ethylene -5, 5'- bibenzimidazole) membranes.

Differential Scanning Calorimetric (DSC) measurements were performed on DSC-Q10 TA instrument at a heating rate of 10 $^{\circ}$C min^{-1} under nitrogen purge of 50 ml min^{-1}. 3-6 mg of samples in sealed aluminium pans were used. The heat-cool-reheat programme was applied for the DSC measurements. Thermogravimetric Analysis (TGA) was performed on STA 6000 Perkin Elmer instrument to study thermal degradation behaviour of PBIE. 3-8 mg of samples were heated from 30 $^{\circ}$C to 900 $^{\circ}$C at a heating rate of 10 $^{\circ}$C min^{-1} in air with gas flow of 50 ml min^{-1}.

Scanning electron microscopy (SEM) was performed on the Quanta 200 3D SEM at low vacuum mode in the range of 0-200 Pa, operating at 20 kV using Large Field Detector (LFD). To capture better images the samples were sputter coated with 10 nm thick layer of gold using a Polaron SC 6420 sputter coater. Virgin and UV irradiated samples were

scanned at various resolutions. Contact angle measurements were performed on the RAME-HART NRL-Model CA goniometer instrument fitted with Cannon camera. Deionized water was used and the measurements were performed in triplicate. Rigaku Dmax 2500 diffractometer was used for wide angle X-ray diffraction (WAXD) measurements. Cu Kα wavelength was used for all the measurements. The generator was operated at 40 kV and 150 mA. Samples were scanned in the diffraction angle (2θ) range of 5° to 90° with a scan rate of 4° min^{-1}.
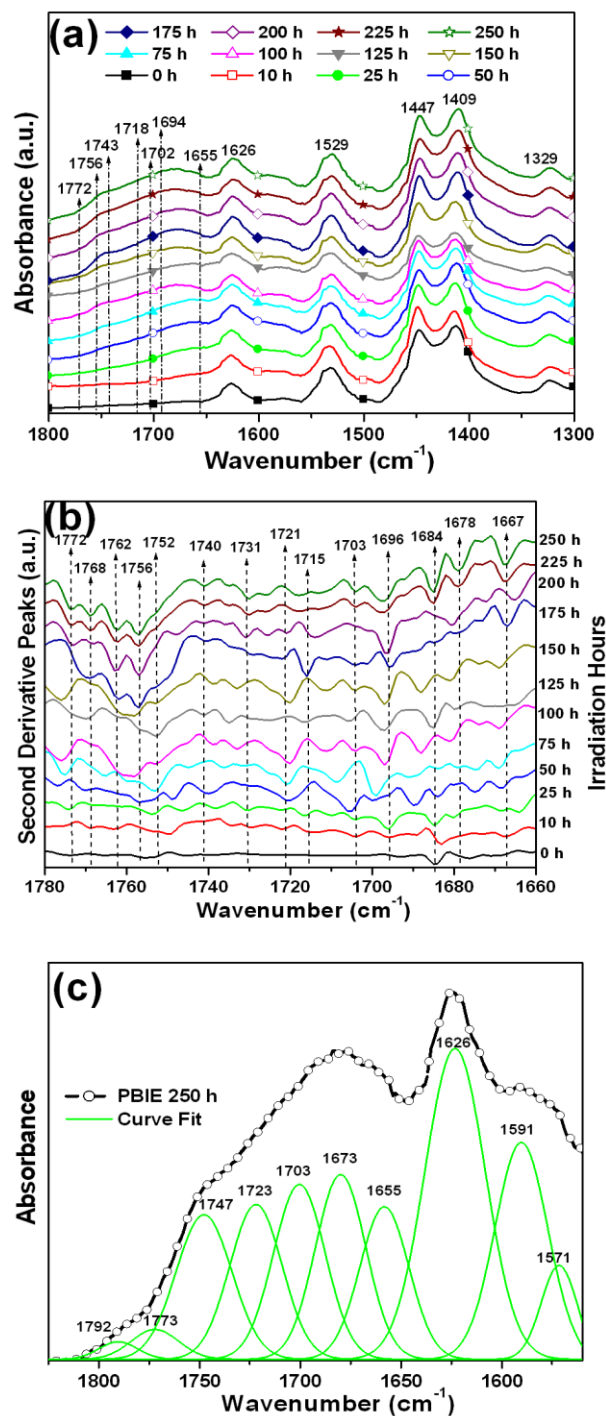

Fig. 3. (a) FTIR ATR spectra of PBIE membranes showing absorption in the carbonyl region (b) Second differential of FTIR ATR spectra of PBIE showing absorbance in the carbonyl region (c) Fitted FTIR ATR spectra of PBIE in the carbonyl region after 250 h of UV irradiation.

Results and discussion

Oxidative degradation of PBIE membranes

FTIR spectroscopy is best suited for the real-time analysis of polymer degradation [32, 33]. It is well known that UV radiations have sufficient energy for bond scissions and degradation processes proceed *via* free radical generation. FTIR ATR spectra of virgin and photo-irradiated samples of the PBIE from 3620 - 780 cm^{-1} range are shown in **Fig. 2**.
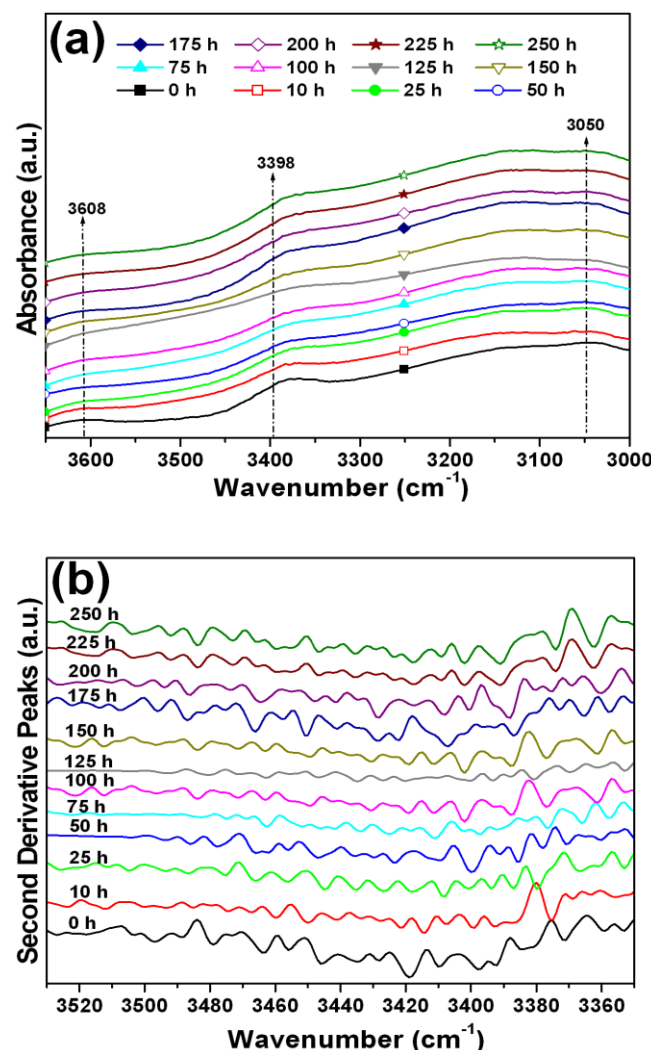

Fig. 4. (a) FTIR spectra of PBIE membranes showing absorption in the hydroxyl region (b) Second differential of FTIR spectrum of poly(2,2'-ethylene -5,5'-bibenzimidazole) PBIE showing absorbance peaks in the hydroxyl region (3530 cm^{-1} to 3350 cm^{-1}).

The formation of various byproducts containing carbonyl groups like ketones, acids, esters and hydroxides along with hydro peroxides have been observed during photodegradation of polymers [30, 34]. This is clearly reflected in the FTIR spectra of photo irradiated PBIE samples in the carbonyl region (**Fig. 3a**). No peaks were observed for carbonyl group in 1670 - 1800 cm^{-1} range for virgin PBIE, while gradual evolution of the broad peak was observed with photo-irradiation. The evolution of broad stretching peak in the carbonyl region (1670 - 1800 cm^{-1}) is an evidence of oxidative photodegradation of PBIE

polymer [19]. The second derivative of the FTIR ATR spectrum of the samples strongly supports the formation of various carbonyl functionalized groups (**Fig. 3b**). The strong signals at 1673 cm^{-1}, 1686 cm^{-1}, 1703 cm^{-1} and 1718 cm^{-1} correspond to the C=O stretching vibrations of ketones and carboxylic acids which were formed as a result of photo irradiation [35].

The formation of the carbonyl functional groups promotes chain scissions, which may result in the lowering of molecular weight. The peak at 1626 cm^{-1} is attributed to C=C and C=N stretching vibrations of aromatic rings [15, 18, 36]. The peak at 1329 cm^{-1} is assigned to the C−N stretching vibrations of aromatic tertiary amines [37]. The strong to weak signals observed in the range 1725 − 1743 cm^{-1} is attributed to the formation of a small amount of aldehyde terminated chains. The absorption peaks in the range 1770 − 1810 cm^{-1} were assigned to the formation of the aryl carbonates. The peaks in the carbonyl region (**Fig. 3c**) are attributed to the formation of polar functional groups [38]. The absorption peak at 1636 cm^{-1} is attributed to O-H bending vibrations. The peak at 1655 cm^{-1} is assigned to ketones with conjugation or quinine like structures or amides.
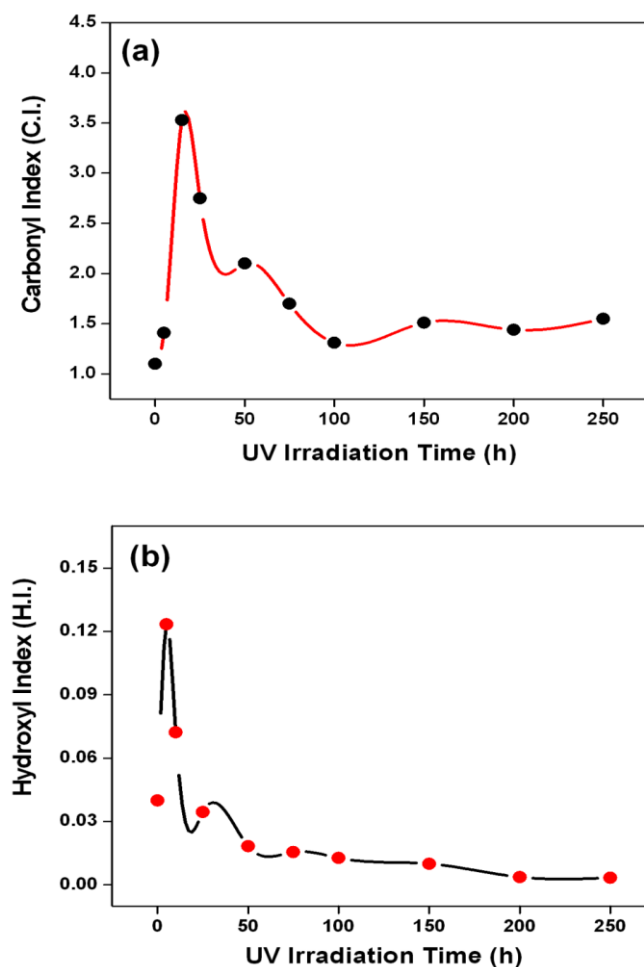

Fig. 5. Growth of (a) carbonyl (C.I.) and (b) hydroxyl indexes (H.I.).

Similar changes may be observed in the hydroxyl region also. FTIR spectrum (**Fig. 4a** and **b**) shows growth of hydroxyl peak and its second derivatives. The peaks at

2920 cm^{-1} and 2850 cm^{-1} correspond to the asymmetric and symmetric C-H stretching vibrations, respectively, which belong to the aliphatic methylene group of PBIE. The decrease in the intensity of these C-H stretching vibrational peaks was observed due to the photodegradation of PBIE membranes. The intensity and broadness of signals in the carbonyl and hydroxyl region was found to increase with increase in the time of UV irradiation which is an evidence of the formation of wide range of functional groups like ketones, ethers, esters, acids and hydroxyls [30]. Additionally, peak at 3608 cm^{-1} in irradiated samples is attributed to the O-H stretch of hydroxyl groups which showed increase in the absorbance with the increase in UV irradiation time [31, 39]. The hydroxyl index (H.I.), may be explained as the ratio of the absorbance at two different wave numbers (A_{3510} / A_{860}) while the carbonyl index (C.I.) may be defined as the ratio of absorbance at two different wave numbers (A_{1715} / A_{860}).
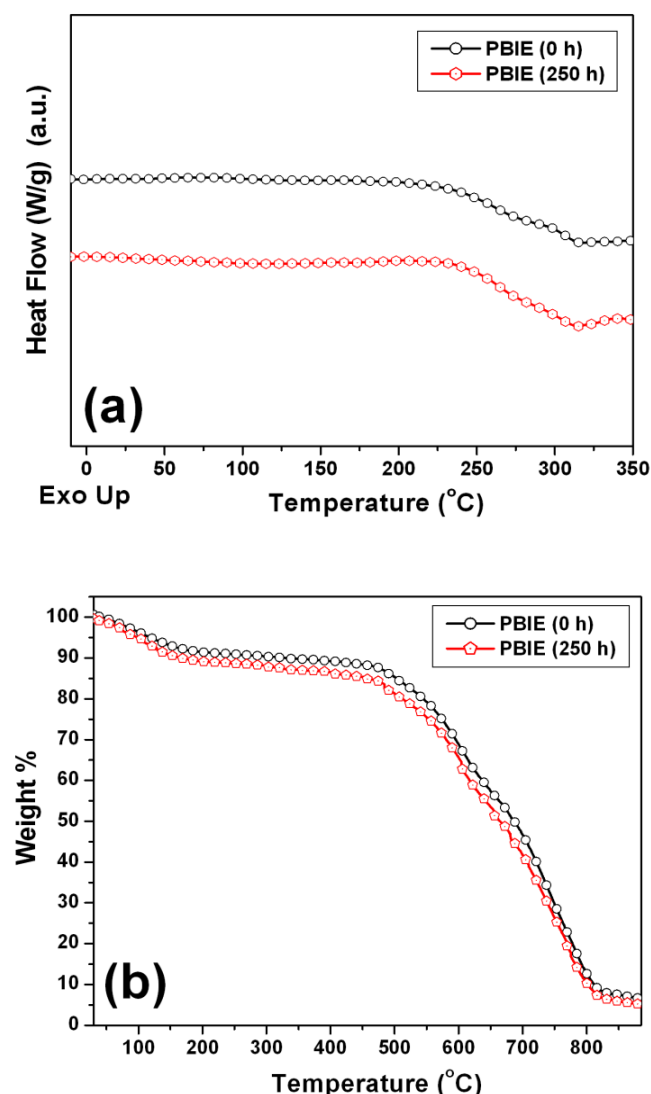

(a)

(b)

Fig. 6. Thermal analysis of PBIE, before and after UV irradiation (a) DSC thermogram of PBIE (in nitrogen) and (b) TGA thermogram of PBIE (in air).

The hydroxyl index (H.I.) and carbonyl index (C.I.) increased as a function of irradiation time (**Fig. 5a** and **b**) up to initial 50 hours and then tend to decrease till 250

hours of irradiation. This shows that maximum absorption of radiation takes place because of the presence of large number of unsaturated bonds which later tend to reduce in number due to photo-oxidation and hence the absorption.

The C. I. also reveals that the maximum surface oxidation occurred within few hours hence the carbonyl groups formed initially are either transformed to other functional groups or cross-linked or degraded on prolonged irradiation. The broad signal in the 3350 cm^{-1} to 3430 cm^{-1} range with a peak maximum at 3398 cm^{-1} is assigned to non-hydrogen bonded N-H stretching vibrations as observed in their second derivatives. The signal at 3145 cm^{-1} is attributed to the N-H stretching vibrations, which occur due to N-H-N hydrogen bonding. Aromatic C-H stretching vibrational signal is observed at 3050 cm^{-1}. The current approach is highly effective in predicting degradation results in very short time. Photoirradiation results are also in accordance with the results of other degradation methods.

Thermal properties of PBIE membranes

The thermal transitions occurring in amorphous and crystalline polymers have been discussed at length [40-43]. DSC analyses of virgin and irradiated PBIE samples revealed its amorphous nature and T_g was clearly observed as an endothermic heat flow curve (**Fig. 6a**). It is evident from the graph that virgin PBIE shows two different T_g transitions at 257 °C and 310 °C. These two different T_g values may be attributed to the incompatibility between aromatic and aliphatic segments of the polymer chains. The lower T_g corresponds to the aliphatic segments whereas higher T_g to the aromatic segments. The lowering in T_g may also be observed with the increase in UV irradiation time. This may be attributed to the chain scissions and partial change in aromatic rings of polymer due to photo-oxidation [44]. The T_g values showed overall lowering in T_g of PBIE with increase in UV irradiation time and summarized in **Table 1**. In the case of 250 h irradiated samples, the increase in the lower T_g value from 257 °C to 266 °C may be attributed to the increased chain stiffening resulting from the association of the formed functional groups on aliphatic segments. On the other hand, the marginal lowering in the higher T_g value from 310 °C to 305 °C may be attributed to reduction of interchain interactions of aromatic segments.

Table 1. DSC, TGA and inherent viscosity data obtained for PBIE membrane.

Irradiation Time	T_{g1}	T_{g2}	WLT	IDT	η_{inh}
(h)	(°C)	(°C)	(°C)	(°C)	(dL g^{-1})
0	257	310	185	450	0.96
250	266	305	205	415	0.89

The degradation behaviour of virgin and photo-irradiated films in air is clearly observed in TGA curves (**Fig. 6b**). It may be observed that water loss temperature (*WLT*) differs in both cases (**Table 1**). This may be attributed to the change in the PBIE affinity towards water due to photo-oxidation. Further, virgin polymer exhibited an initial decomposition temperature (*IDT*) of 450 °C which is observed to decrease to 415 °C in 250 h UV treated

polymer films. This may be attributed to the change in molecular structure and molecular weight of PBIE as a result of free radical oxidative degradation. The change in thermal behaviour of polymers as a function of molecular weight has been described by Grassie et al [45]. Viscosity measurements showed a minor decrease in the inherent viscosity of PBIE during photo-irradiation process. The decrease in η_{inh} (**Table 1**) may be directly related to the decrease in the molecular weight of the polymer.
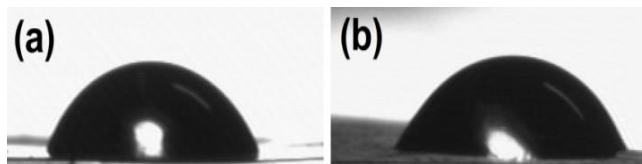
Fig. 7. Contact angle pictures of PBIE (a) before UV irradiation and (b) after 250 h UV irradiation.

Table 2. Contact angle measurement data of PBIE membrane.

Irradiation Time (h)	Contact Angle (in degree)
0	72
100	69
200	65
250	63
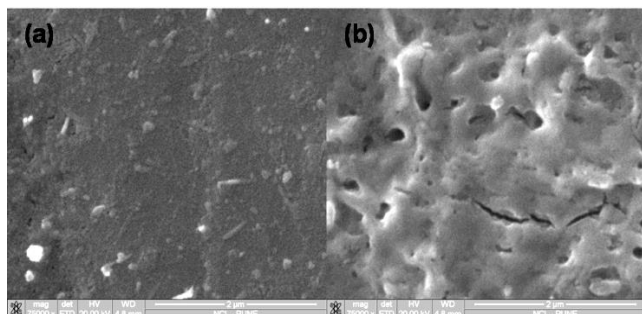
Fig. 8. SEM images of PBIE (a) before UV irradiation and (b) after 250 h UV irradiation.

Surface analysis of PBIE

Contact angle measurements are significant from the perspectives of the adsorption kinetics and surface energy changes [46]. Contact angle measurements are also applicable in determining the material's surface affinity towards liquids [47]. For the virgin and 250 hour UV irradiated samples, the contact angles of 72° and 63° were observed (**Fig. 7a and b**). From the contact angle observations, it may be concluded that the contact angle decreases with increasing irradiation time in PBIE membranes. These results also confirm that there is an increase in the hydrophilic behaviour of PBIE films after UV treatment, which may be attributed to the formation of polar functional groups on the exposed polymer surfaces [48, 49]. The contact angle values are summarized in **Table 2**. These results are in agreement with the results obtained by FTIR spectroscopy.

Scanning electron microscopy was used to study the morphological changes on the surface of the membranes due to the UV irradiation of PBIE films [50]. Surface damages were not observed prior to UV irradiation whereas nano cracks, fractures and holes were observed after photo

degradation (**Fig. 8a** and **b**). From the development of these nano structures it may also be concluded that PBIE polymer surface becomes rough and may be subjected to mechanical and chemical degradations [51, 52]. There may be remarkable loss in the mechanical properties of the membranes on prolonged radical attack under oxidizing environments which may further result in severe performance degradation of polymer membranes [19, 53, 54]. The increased roughness on the surface may also be partially responsible for changes in contact angles described above. SEM results obtained are supported by contact angle measurements and FTIR results. The contact angle measurements and SEM results provide extremely useful information about the surface degradation on the membrane. The present photodegradation study has advantage to other studies because in it surface changes occur only due to irradiation, hence degradation effects of the other factors like solvents, impurities and humidity may be overcome.
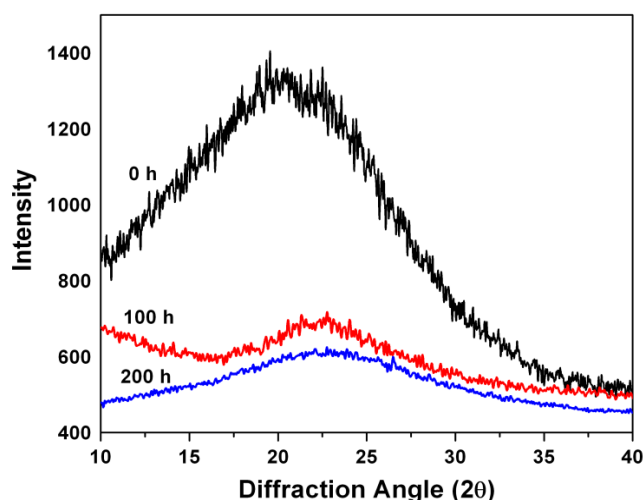

Fig. 9. The WAXD traces of poly (2, 2'- ethylene -5, 5'-bibenzimidazole) taken at 0, 100 and 200 h of photoirradiation.

Wide angle X-ray diffraction (WAXD) analysis of PBIE

Wide angle X-ray diffraction patterns indicate amorphous nature of PBIE polymer films. In the WAXD plots of the samples it was observed that the intensity of peak maxima at $2\theta = 21.0°$ decreased with increased irradiation time (**Fig. 9**). This may be attributed to the destruction of some packed regions in the PBIE polymer [55, 56]. Also, the shift in peak maxima from $2\theta = 21.0°$ to higher Bragg's diffraction angle $2\theta = 23.1°$ was observed. This shift in Bragg's diffraction angle is due to the lowering of d-spacing (d_{sp}) from 4.29 Å in virgin PBIE to 3.92 Å in degraded PBIE (**Table 3**).

Table 3. WAXD data obtained for PBIE membrane.

Irradiation Time (h)	Diffraction Angle (2θ) (At peak maxima)	d-spacing (d_{sp})
0	21.0	4.29
100	22.8	3.98
200	23.1	3.92

The reduction in d_{sp} may be attributed to the consequence of random chain scissions occurring during

photoirradiation by the attack of free radicals [56]. In the case of virgin PBIE membranes, H-bonding between imidazole units results in lower d-spacing [31]. After 100 h of irradiation, there is no significant change in either amorphous peak maxima or d_{sp} in the PBIE samples observed.
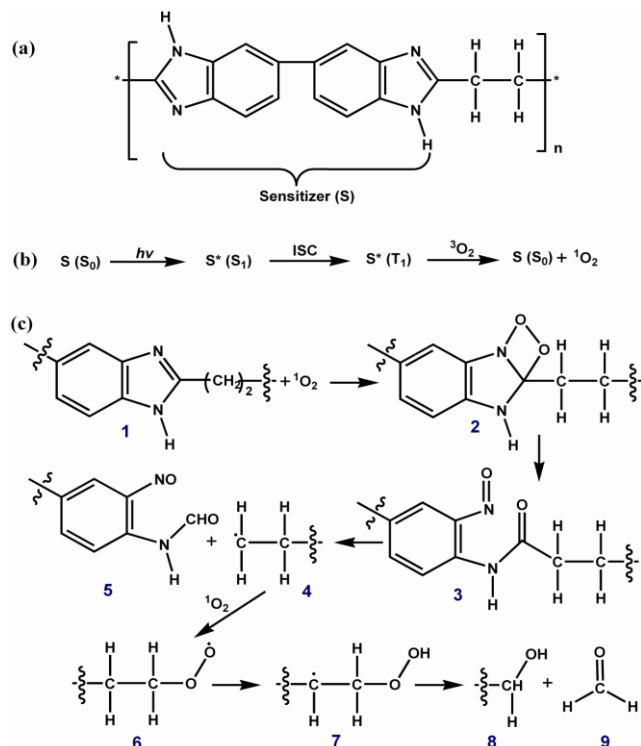

Fig. 10. Proposed mechanism of photo-oxidative degradation of PBIE, (a) benzimidazole units acting as sensitizer in oxidative degradation, (b) generation of singlet state oxygen from triplet state molecular oxygen with the help of benzimidazole units (c) detailed mechanism of photo-oxidative degradation of PBIE under the influence of polychromatic UV rays.

Degradation mechanism of PBIE

FTIR results suggest photo-oxidative degradation of PBIE membranes. To explain this, a degradation mechanism of PBIE based on the FTIR results is being proposed. It is known that the triplet state of molecular oxygen ($^3O_2$) is not effective as an oxidizing agent. Only singlet state ($^1O_2$) may act as strong oxidizing species. The fundamental problem is to generate singlet oxygen in order to oxidize the polymer. The singlet oxygen may be generated by the use of sensitizers, which may transfer energy to molecular oxygen from their triplet excited state. The transferred energy must be sufficient enough to pair the unpaired electrons of the triplet state oxygen ($^3O_2 \rightarrow {}^1O_2$).

In the proposed mechanism as shown, we assume that the benzimidazole unit of PBIE acts as sensitizer and facilitates the generation of singlet state oxygen ($^1O_2$) from the triplet state of the molecular oxygen ($^3O_2$) (**Fig. 10 a and b**). Since the polymer chains contain a number of benzimidazole units (**1**), there may always be an excess of sensitizing activity in the presence of UV light. Under such circumstances, the highly reactive singlet state oxygen ($^1O_2$) may selectively react with the more substituted imidazole part of the benzimidazole unit to give very unstable bicyclic

peroxide adducts (**2**). These adduct with four member non aromatic heterocyclic rings with peroxide linkage and high angle strain may undergo further structural changes (**Fig. 10 c**).

The cyclic peroxide (**2**) may immediately transform into adduct (**3**) by undergoing concerted reaction mechanism. This is a more stable intermediate having free nitrosyl and ketone groups formed due to cleavage of two fused rings. The formation of this intermediate is in accordance with the FTIR results and may be easily observed in **Fig. 2** showing growth as the carbonyl absorption. It is further supported by the carbonyl index, which gives clear indication of carbonyl growth over a period of time. The carbonyl groups are known to promote chain scissions, which further reduce molecular weight of the polymer. Thus adduct (**3**) promotes chain scission of the polymer which results in an unstable carbon radical intermediate (**4**) and a more stable, low molecular weight aldehyde terminated aromatic adduct (**5**). This carbon free radical further propagates to give peroxide radical intermediate (**6**) after reacting with the singlet state molecular oxygen. This peroxide radical-terminated adduct may get stabilized by hydrogen abstraction from the adjacent carbon atom resulting in the formation of a more stable carbon radical intermediate (**7**). The carbon radical intermediate (**7**) may rearrange to give more stable alcohols (**8**) and ketones (**9**). The proposed mechanism is in agreement with the characterization data. The formation of various oxidation products in detail is also proposed in the mechanism.

Conclusion

From the present photo degradation study of PBIE membranes, it may be concluded that PBI polymer degrades by an oxidative mechanism of degradation. Major changes were observed in the carbonyl region of the FTIR spectrum. Contact angle measurements are in agreement with FTIR results and show a decrease in contact angle and an increase in surface energy due to the formation of polar functional groups on the surface of PBIE membranes. The thermal degradation study indicated a lowering of the degradation temperature which was attributed to the lowering of molecular weight as a result of chain scissions in polymer. SEM results showed development of nano fractures, nano cracks and holes. WAXD analysis showed gradual shift of broad diffraction peak maxima towards higher diffraction angle which indicates amorphous nature of the degraded polymer. Based on these observations, a degradation mechanism has been proposed. Since, the results obtained by UV irradiation of PBIE are in accordance with those reported by thermal and chemical degradation, it is concluded that photo (UV) degradation may be used as a suitable method to study the accelerated degradation of polymers applicable in fuel cells, gas separations and other high performance applications. These results indicate that UV irradiation process may also be used for surface modification of PBIE membranes.

Reference

1. Vasile C., Popa V.I., Paun A., Sabliovschi M. *Cell Chem Technol* **1995**, 29, 361.
2. Moore C.J. *Environ Res* **2008**, 108, 131.
   DOI: 10.1016/j.envres.2008.07.025
3. Oehlmann J., Oetken M., Schulte-Oehlmann U. *Environ Res* **2008**, 108, 140.
   DOI: 10.1016/j.envres.2008.07.016
4. Talsness C.E. *Environ Res* **2008**, 108, 158.
   DOI: 10.1016/j.envres.2008.08.008
5. Vom S.F.S., Parmigiani S., Palanza P.L., Everett L.G., Ragaini R. *Environ Res* **2008**,108,127.
   DOI: 10.1016/j.envres.2008.03.008
6. Andrews E.H. *Brit Polym J* **1978**, 10, 39.
   DOI: 10.1002/pi.4980100108
7. Kumar A.P., Depan D., Tomer S. N., Singh R.P. *Prog Polym Sci* **2009,** 34, 479.
   DOI: 10.1016/j.progpolymsci.2009.01.002
8. Manceau M., Rivaton A., Gardette J.L. *Macromol Rapid Commun* **2008**, 29, 1823.
   DOI: 10.1002/marc.200800421
9. Rivaton A., Gardette J.L. *Polym Degrad Stabil* **1999**, 66, 385.
   DOI: 10.1016/S0141-3910(99)00092-0
10. Devanathan R. *Energ Environ Sci* **2008**, 1, 101.
    DOI: 10.1039/B808149M
11. Bose S., Kuila T., Nguyen T.X.H., Kim N.H., Lau K., Lee J.H. *Prog Polym Sci* **2011**, 36, 813.
    DOI: 10.1016/j.progpolymsci.2011.01.003
12. Carollo A., Quartarone E., Tomasi C., Mustarelli P., Belotti F., Magistris A., et al. *J Power Sources* **2006,** 160, 175.
    DOI: 10.1016/j.jpowsour.2006.01.081
13. Jang W., Lee C., Sundar S., Shul Y.G., Han H. *Polym Degrad Stabil* **2005,** 90, 431.
    DOI: 10.1016/j.polymdegradstab.2005.04.012
14. Lin H.L., Hsieh Y.S., Chiu C.W., Yu T.L., Chen L.C. *J Power Sources* **2009,** 193, 170.
    DOI: 10.1016/j.jpowsour.2009.01.062
15. Modestov A.D., Tarasevich M.R., Filimonov V.Y., Zagudaeva N.M. *Electrochim Acta* **2009**, 54, 7121.
    DOI: 10.1016/j.electacta.2009.07.031
16. Yan W-M., Chu H-S., Lu M-X., Weng F-B., Jung G-B., Lee C-Y. *J Power Sources* **2009,** 188, 141.
    DOI: 10.1016/j.jpowsour.2008.11.107
17. Li Q., Jensen J.O., Savinell R.F., Bjerrum N.J. *Prog Polym Sci* **2009,** 34, 449.
    DOI: 10.1016/j.progpolymsci.2008.12.003
18. Kumbharkar S.C., Islam M.N., Potrekar R.A., Kharul U.K. *Polymer* **2009,** 50, 1403.
    DOI: 10.1016/j.polymer.2009.01.043
19. Chang Z., Pu H., Wan D., Liu L., Yuan J., Yang Z. *Polym Degrad Stabil* **2009,** 94, 1206.
    DOI: 10.1016/j.polymdegradstab.2009.04.026
20. Kopitzke R.W., Linkous C.A., Nelson G.L. *Polym Degrad Stabil* **2000**, 67, 335.
    DOI: 10.1016/S0141-3910(99)00135-4
21. Liu G., Zhang H., Hu J., Zhai Y., Xu D., Shao Z. *J Power Sources* **2006**, 162, 547.
    DOI: 10.1016/j.jpowsour.2006.07.008
22. Musto P., Karasz F.E., MacKnight W.J. *Polymer* **1993**, 34, 2934.
    DOI: 10.1016/0032-3861(93)90618-K
23. Musto P., Wu L., Karasz F.E., MacKnight W.J. *Polymer* **1991**, 32, 3.
    DOI: 10.1016/0032-3861(91)90554-V
24. Kumbharkar S.C., Kharul U.K. *Eur Polym J* **2009,** 45, 3363.
    DOI: 10.1016/j.eurpolymj.2009.10.006
25. Mendes A.A., Cunha A.M., Bernardo C.A. *Polym Degrad Stabil* **2011**, 96, 1125.
    DOI: 10.1016/j.polymdegradstab.2011.02.015
26. Hill D. J. T., O'Donnell J. H., Pomery P. J. Fundamental Aspects of Polymer Degradation by High-Energy Radiation. *Materials for Microlithography: American Chemical Society* **1985**.
    DOI: 10.1021/bk-1984-0266.ch004
27. Ghaemy M., Scott G. *Polym Degrad Stabil* **1981,** 3, 233.
28. Lobato J., Caizares P., Rodrigo M.A., Linares J.J., Manjavacas G. *J Membrane Sci* **2006**, 280, 351.
    DOI: 10.1016/j.memsci.2006.01.049
29. Andrady A.L., Hamid S.H., Hu X., Torikai A. *Photochem Photobiol B: Biol* **1998**, 46, 96.
30. Feldman D. *J Polym Environ* **2002**, 10, 163.
    DOI: 10.1023/A:1021148205366
31. Bhavsar R.S., Nahire S.B., Kale M.S., Patil S.G., Aher P.P., Bhavsar R.A., et al. *J Appl Polym Sci* **2011,** 120, 1090.
    DOI: 10.1002/app.33246
32. Celina M., George G.A. *Polym Degrad Stabil* **1995,** 48, 297.
    DOI: 10.1016/0141-3910(95)00053-O
33. George G.A., Celina M., Vassallo A.M., Coleclarke P.A. *Polym Degrad Stabil* **1995,** 48, 199.
    DOI: 10.1016/0141-3910(95)00035-K
34. Mahon A., Kemp T.J., Coates R.J. *Polym Degrad Stabil* **1998**, 62, 15.
    DOI: 10.1016/S0141-3910(97)00255-3
35. Chang Z., Pu H., Wan D., Jin M., Pan H. *Polym Degrad Stabil* **2010,** 95, 2648.
    DOI: 10.1016/j.polymdegradstab.2010.07.009
36. Sroog C.E. Polyimides. *Prog Polym Sci* **1991,** 16, 561.
37. Silverstein R.M. David F.X.W., Kiemle J. Spectrometric identification of organic compounds. John Wiley & Sons, **2005**.
38. Ning Y-C. Interpretation of Organic Spectra. John Wiley & Sons, **2011**.
39. Gerwert K., Kötting C. Fourier Transform Infrared (FTIR) Spectroscopy. eLS: John Wiley & Sons, **2001**.
    DOI: 10.1002/9780470015902.a0003112.pub2
40. Meischner C., Greiner B., Hauptmann P., Donth E. *Acta Polymerica* **1986,** 37, 453.
41. Allegra G., Bignotti F., Gargani L., Cociani M. *Macromolecules* **1990,** 23, 5326.
    DOI: 10.1021/ma00228a004
42. Mark J.E. Physical Properties of Polymers Handbook. Springer. **2006**.
43. Sperling L.H. Introduction to Physical Polymer Science. John Wiley & Sons, **2006**.
44. Kishore V. Pochiraju G.P.T., Gregory A.. Schoeppner. Long-Term Durability of Polymeric Matrix Composites. Springer. **2011**.
45. Norman G. S. Polymer Degradation and Stabilisation. CUP Archive. **1988**.
46. Mattioli S., Kenny J.M., Armentano I. *J Appl Polym Sci* **2012,** 125, E239.
    DOI: 10.1002/app.36827
47. Zereshki S., Figoli A., Madaeni S.S., Simone S., Jansen J.C., Esmailinezhad M., et al. *J Membrane Sci* **2010**, 362, 105.
    DOI: 10.1016/j.memsci.2010.06.025
48. Kafi A.A., Chen Z., Dai X.J., Fox B.L., Lamb P.R., Wang X. *Nanosci Nanotechnol Lett* **2012**, 4, 344.
    DOI: doi.org/10.1166/nnl.2012.1315
49. Luo S-C., Sekine J., Zhu B., Zhao H., Nakao A., Yu H-H.. *Acs Nano* **2012**, 6, 3018.
    DOI: 10.1021/nn300737e
50. Zaldivar R.J., Nokes J.P., Patel D.N., Morgan B.A., Steckel G., Kim H.I. *J Appl Polym Sci* **2012**, 125, 2510.
    DOI: 10.1002/app.36350
51. Ferreira F.G.D., Lima M.A.G.A., Almeida Y.M.B., Vinhas G.M. *Polimeros* **2009**, 19, 313.
    DOI: 10.1590/S0104-14282009000400011
52. Ruch D., Becker C., Riche A., Etienne S., Bour J. *Polym Sci Ser A* **2008** 50, 716.
    DOI: 10.1134/S0965545X08060163
53. Davis R., Chin J., Lin C-C., Petit S. *Polym Degrad Stabil* **2010,** 95, 1642.
    DOI: 10.1016/j.polymdegradstab.2010.05.029
54. Schlick S., Kruczala K. Advanced ESR methods in polymer research: John Wiley & Sons, **2006**.
    DOI: 10.1002/047005350X.ch9
55. Delgado A.O., Rizzutto M.A., Severin D., Seidl T., Neumann R., Trautmann C. *Nucl Instrum Meth B* **2012,** 273, 55.
    DOI: 10.1016/j.nimb.2011.07.037
56. Tripathy S.P., Mishra R., Dwivedi K.K., Khathing D.T., Ghosh S., Fink D. *Radiat Eff Defect S* **2002**, 157, 303.
    DOI: 10.1080/10420150212993

At the top of column 2 (above entry 28):
DOI: 10.1016/0141-3910(81)90037-9