

OXIDATIVE RESISTANCE OF BIMODAL HDPE AND SILANE CROSSLINKED BIMODAL HDPE UNDER EXPOSURE TO HOT CHLORINATED WATER

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Abstract. Experiments were performed in an attempt to identify the reactive intermediate(s) involved in the degradation of bimodal HDPE (B-HDPE) and silane crosslinked bimodal HDPE (SXB-HDPE) in chlorinated water. These studies, demonstrated that chlorination is one reaction that ultimately contributes to HDPE degradation. In this case, the intermediates involved could either be Cl_2 or NaOCl . Available information also indicates that, for many polymers, free chlorine, chemically generated from NaOCl , could likewise be involved as an intermediate in a degradation reaction. Thus, tests were undertaken to specifically address this latter issue with respect to HDPE degradation. The degradation of HDPE was monitored under a variety of conditions by DSC and FT-IR spectroscopy. Furthermore, the effect of hot chlorinated solution on mechanical properties was investigated by performing drop impact and tensile tests on unexposed and exposed specimens. Surface inspection was being carried out using SEM. The rate of degradation was found to be temperature and time dependent, and degradation was most pronounced at temperature $>50^\circ\text{C}$ and the time duration >500 hours. DSC showed that a small increase in crystallinity, melting point and melting peak broadening of the samples subjected to more severe chlorine oxidative treatment. The FTIR experiments showed formation of carbonyl groups. Moreover, FTIR measurements suggested that transformation of the hydroxyl groups leads to a weakening of the overall hydrogen bonding strength in the degraded samples. The data strongly pointed to Cl_2 as the key intermediate in the surface oxidative degradation.

Keywords: Silane crosslinked, chlorinated water, bimodal HDPE, chlorination, Oxidative degradation

Abstrak. Eksperimen telah dijalankan untuk mengenalpasti elemen perantaraan yang reaktif dalam degradasi bimodal HDPE (B-HDPE) dan bimodal HDPE bersambung-silang (SXB-HDPE) dalam air berklorin. Kajian menunjukkan pengklorinan merupakan faktor penyumbang terhadap degradasi HDPE. Dalam kes ini, media perantaraan kemungkinan ialah Cl_2 atau NaOCl . Maklumat menunjukkan bagi kebanyakan polimer, 'klorin bebas' yang terhasil daripada tindak balas kimia NaOCl merupakan media perantaraan dalam tindak balas degradasi. Oleh itu, ujikaji DSC dan spektroskopi FTIR dijalankan pada keadaan yang berbagai untuk mengenalpasti degradasi HDPE. Kesan 'larutan berklorin panas' terhadap sifat mekanikal polimer turut juga dikaji, antaranya ialah ujian ketegasan dan ujian hentaman impak terhadap sampel yang mengalami proses pengoksidaan klorin dan tanpa pengoksidaan klorin. Kajian terhadap permukaan sampel degradasi dijalankan dengan SEM. Kadar degradasi didapati berkadaran dengan suhu dan masa. Kadar degradasi paling nyata pada suhu $>50^\circ\text{C}$ dan masa >500 jam. DSC menunjukkan terdapat sedikit peningkatan terhadap tahap pengkristalan, suhu peleburan kristal dan suhu peleburan puncak bagi sampel yang mengalami kesan pengklorinan yang kritikal. Ujian spektroskopi FTIR menunjukkan kemunculan kumpulan berfungsi karbon pada sampel yang mengalami degradasi. Spektroskopi FTIR menunjukkan transformasi

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kumpulan hidroksi mengurangkan ikatan hidrogen dalam sampel degradasi. Data ini menunjukkan Cl_2 ialah medium perantaraan dalam degradasi pengoksidaan permukaan.

Kata kunci: Bersambung silane, air berklorin, bermodal HDPE, ujikaji pengklorinan, pengoksidaan degradasi

1.0 INTRODUCTION

Many manufacturers want to use plastic materials in components of hot potable water systems. However, there is some concern that residual chlorine in treated water may have potential detrimental effects on plastic materials. In cooperation with a manufacturer of residential water system components, a study was undertaken to demonstrate the suitability of bimodal HDPE and crosslinked bimodal HDPE for such service. The performance of bimodal HDPE compounds compared with crosslinked bimodal HDPE was evaluated.

Free chlorine is a strong oxidising agent. It reacts rapidly with various inorganic compounds and more slowly oxidises organic compounds. Oxidation-reduction Potential (ORP) provides a measurement of the oxidising potential of free chlorine contained solution. A higher milivolt reading indicates a greater oxidising potential of the solution [1]. Sodium hypochlorite is one of the solutions containing free chlorine [2].

The use of Cl_2 as disinfectant to kill bacteria and thus make water potable is well established [3]. It is also acknowledged that many polymeric materials in contact with chlorinated water degraded at rates that can adversely influence the properties and, hence, function of the polymer [4-6]. Purification membranes, pipes, and pump parts made from, e.g., polyamides, polyethylene, and polypropylene routinely show the effects of exposure to chlorinated water that, in turn, often requires replacement of these items at more frequent intervals. In the present context, degradation means any change at the molecular level that alters the properties of the polymer. Low levels of degradation can influence properties such as elasticity and permeability, whereas high levels of degradation can result in loss of material and the formation of sizable cracks in molded samples.

In order to describe "chlorinated water" accurately, it is necessary to specify the pH of the system and to consider the equilibrium equation.



It is then appropriate to consider the pH-dependent concentration profiles of three species, in particular Cl_2 , HClO , and ClO^- , which have been measured spectroscopically [7]. Alkaline systems are characterised by a high concentration of ClO^- , which rapidly drops to zero as the pH is lowered from ca. 9 to 8. As the system is further acidified, and the pH lowered through ca. 8, the concentration of hypochlorous acid, HClO , correspondingly increases. The latter reaches a maximum at pH ca. 5

and, thereafter, decreases upon further acidification. At the same time, upon acidification, and beginning at pH ca. 7, the concentration of Cl_2 increases slowly. At pH values less than ca. 5, the equilibrium of Eqn.1 shifts to the left, and the decrease in HClO concentration is accompanied by a further increase in the concentration of Cl_2 . Thus, at a pH of ca. 7, “chlorinated water” is characterised by a high concentration of HClO and a low concentration of Cl_2 . At pH values less than ca. 4, the reverse holds, and “chlorinated water” is characterised by a high concentration of Cl_2 and a low concentration of HClO.

2.0 EXPERIMENTAL PROCEDURE

2.1 Bottles Preparation

Boston round bottles of 500 ml size were blow-molded by an extrusion blow-molding machine (Magic Inc., 38 mm diameter) at 180°C and mold temperature of 25°C. The bottles were 30 g in weight and have 1 cm wall thickness. The bottle is blow-molded from two different types of high-density polyethylene resins. The information for the HDPE used in this research is shown in Table 1.

Table 1 Specifications for the HDPE materials and chemical

Materials	Description
Titanzex HB 6200	Bimodal HDPE, Density 0.956 g/cm ³ , Melt index 0.35 g/10 min
Crosslinkable bimodal HDPE	Crosslinkable bimodal HDPE, Density 0.956 g/cm ³ , Melt index 0.35 g/10 min
Sodium hypochlorite, solution NaOCl	Molecular weight 74.44, Density 1.206 g/cm ³ , boiling point 111°C, Chlorine content 10-13 %.
Deionized water	pH 7.
Hot chlorination solution	pH = 7.65 + 0.2, Free chlorine content = 10.0 + 0.2 ppm, ORP (mV) = > 850

2.2 Preparation of hot chlorinated solution test on bottles

The oxidative test was conducted by filling the bottles to one third-capacity with deionized water. The filled bottles were then capped and placed on tray in a water bath (Mettler Co, Model WB/OB 10) at 50°C and 70°C. Daily visual inspections were used to monitor the bottles for failures. The external surface of the bottles was exposed to the hot chlorination solution with 10.0 ± 0.2 ppm active free chlorine. The interval time used was 100 hours. This testing was carried out in accordance to the ASTM F2023-00 guidance [1].

3.0 TESTING AND ANALYSIS

Three characterisation techniques, Differential Scanning Calorimetry (DSC), Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) were used to monitor and compare the hot chlorination solution exposed samples to the unexposed sample. The main purpose of these techniques was to characterise qualitatively and quantitatively the variation of both samples.

3.1 Mechanical Testing

Tensile test was performed according to ASTM D638-Type IV [8] and was carried out on an Instron 5576 tensile tester at a crosshead speed of 50 mm min^{-1} and a gauge length of 25 mm. The ultimate stress and ultimate strain of the samples were calculated from the load/displacement curve.

3.2 Drop Impact Test

This test method is used to determine the impact resistance of blow-molded HDPE bottle before and after exposure to the hot chlorinated solution at desired temperature and exposure duration. Drop testing of the water filled bottles conducted by dropping the bottle to strike a hard steel at any angle from one meter height, dropping squarely onto the base or side are specified for the test. Failure is normally defined as “liquid leakage from any part of the bottle after test”. The drop test procedure is defined in testing standards ASTM D 2463-95[9].

3.3 Differential Scanning Calorimetry (DSC) Analysis

Samples were characterised by using Differential Scanning Calorimetry Analysis (Perkin Elmer®, Model DSC 7). Samples of 5–6 mg were encapsulated in aluminium pans and treated at a heating and cooling rates of $10^\circ\text{C min}^{-1}$ in two runs in accordance to ASTM D3417-99 [10]. The temperature range was 25–200°C. The atmosphere used was nitrogen with a flow rate of 20 ml min^{-1} . The onset temperature, melting peak (T_m), and melting enthalpy (Hm) were obtained, and the percentages of crystallinity were determined using the enthalpy of melting for high density polyethylene of 100% crystallinity $H_m = 290 \text{ J/g}$ [11].

3.4 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier Transform Infrared (FTIR) Spectroscopy was used to qualitatively demonstrate the chemical degradation reactions of the hot chlorinated solution on the samples by the occurrence of specific functional groups. Chemical degradation reactions of HDPE sample were characterised using Perkin Elmer Spectrum 2000 Explorer FT-IR Spectrometer at a constant spectral resolution of $R = 0.5 \text{ cm}^{-1}$, in the range

400–4000 cm^{-1} , after acquiring 50 scans. The spectra of the samples investigated were shown in frequency ranges. Structural changes, such as an oxidation level of bimodal HDPE and silane crosslinked bimodal HDPE due to the hot chlorinated solution can be accurately detected by FTIR. All oxidised samples were characterised by the formation of free (non-hydrogen bonded) hydroperoxides (3550 cm^{-1}), free alcohols (3625 cm^{-1}), bonded alcohols and hydroperoxides (3600–3200 cm^{-1}), carbonyl (predominantly strongly overlapped ketones and carboxylic acids, $\sim 1718 \text{ cm}^{-1}$), (γ -Lactones (1770 cm^{-1}) and trans-vinylene bonds (966 cm^{-1})[12].

3.5 Scanning Electron Microscopy

Surface oxidative degradation was investigated using a scanning electron microscopy (SEM), model Philips XL40. Microscope was operated at 10^{-7} Torr vacuum and a 20 kV voltage was employed for imaging the coating surface. The surface on the samples was examined both before and after the hot chlorinated solution immersion tests. The number of voids and crack observed on the tested samples surface were automatically determined from the SEM micrographs.

4.0 RESULTS AND DISCUSSION

4.1 Mechanical Properties

The mechanical tests of samples were carried out to determine ultimate tensile strength and ultimate strain as a function of exposure to hot chlorinated solution with respect to temperature and time. The results are presented in Figures 1 and 2.

Figure 1 illustrates that the ultimate strain decreases slowly with hot chlorinated solution exposure time. After 1000 hours of exposure at 50°C, the strain of bimodal HDPE is reduced from 2798 to 2303% (i.e. relative decrease of 17.7%), followed by silane crosslinked bimodal HDPE, from 1510 to 1423%. Meanwhile, bimodal and silane crosslinked bimodal HDPE after 600 hr exposure to hot chlorinated solution at 70°C (max. 600 h) the strain reduces from 2732 to 2313 and 1510 to 1372%.

Figure 2 shows the variation of ultimate tensile strength with hot chlorinated solution exposure time. Up to 1000 hours of hot chlorinated solution exposure time at 50°C, the ultimate tensile strength of bimodal HDPE decreases from 38.0 to 31.5 MPa, followed by a slight decrease from 24.9 to 22.5 MPa for silane crosslinked bimodal HDPE. However, an accentuate decrease is observed between 500 and 1000 hours.

The bimodal HDPE and silane crosslinked bimodal HDPE exposed to hot chlorinated solution did not exhibit brittle failure, which is characterised by yielding behavior before break. The oxidative process in hot chlorinated solution at 50 and 70°C was demonstrated to be less severe, because of the lower exposed temperature and the absence of oxygen. The bottle still did not show any evidence of degradation

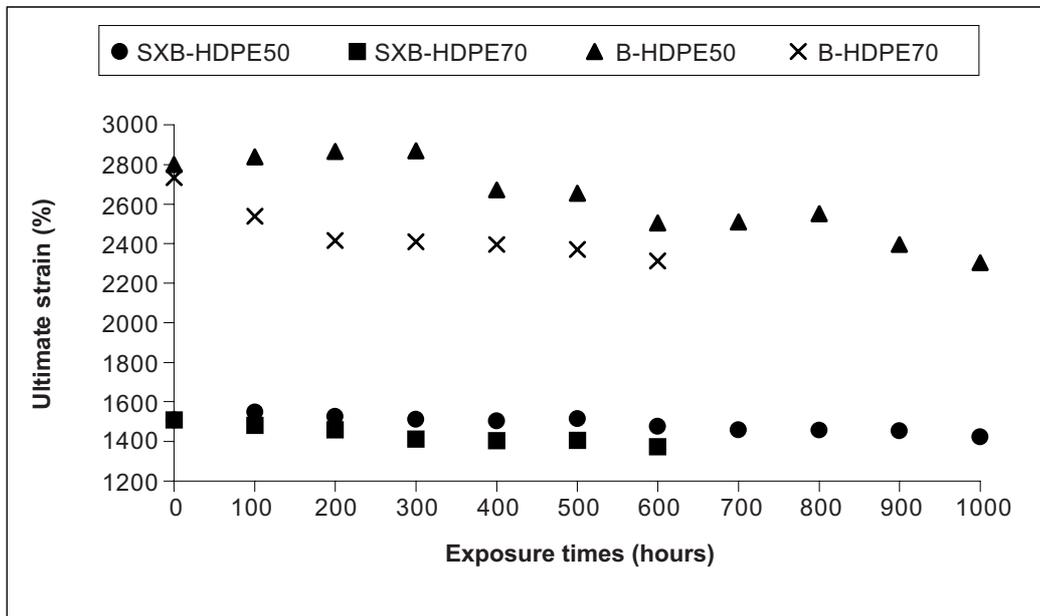


Figure 1 Variation of ultimate strain as a function of hot chlorinated solution exposure time (from 0 to 1000 hr) and different temperature (50 and 70°C)

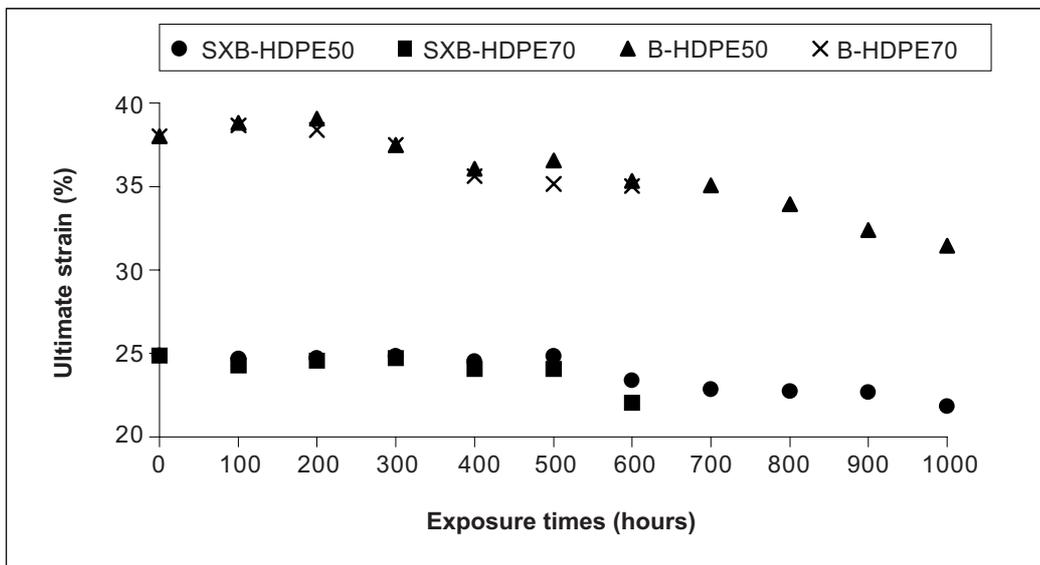


Figure 2 Variation of ultimate strength as a function of hot chlorinated solution exposure time (from 0 to 1000 hr) and different temperatures (50 and 70°C)

after 1000 hr in hot chlorinated solution immersion test, indicating that silane crosslinked bimodal HDPE is thermally stable at that temperature.

From the results the order for the mechanical properties decrement is bimodal HDPE greater than silane crosslinked bimodal HDPE with respect to the ultimate tensile strength and ultimate strain results.

4.2 Drop Impact Resistance Test

The effect of hot chlorinated solution on the impact resistance of HDPE bottles after exposure to the different periods of time is given in Table 2. Bimodal HDPE and silane crosslinked bimodal HDPE exposure to hot chlorinated solution did not show any decrease in impact resistance with an increase in the exposure time and temperature. Meanwhile, no physical fracture or damage was detected. This suggests that the structure property relationship of the base polymer plays an important role in the chemical oxidative property [13].

Table 2 Drop impact test, physical observation after various exposure temperatures and time

Test duration (hours)	Test temperature (°C)	Bimodal HDPE	Silane crosslinked bimodal HDPE
0-1000	50	No crack	No crack
0-600	70	No crack	No crack

4.3 DSC- Changes in Melting Behavior and Crystallinity

Figures 4 to 7 show that the DSC melting curves of bimodal and silane crosslinked bimodal before and after exposure for 1000 hours in hot chlorinated solution. The melting behavior of exposed samples is almost constant. No change in DSC thermogram was observed as shown in Figures 3 to 6. This probably suggests that the crystalline phase did not change with the exposure time and the carbonyl group is concentrated in the amorphous regions.

The melting temperature as a function of exposure time is stated in Table 3. The unexposed bimodal HDPE has lower melting point of 130.93°C as compared with 131.73°C after 1000 hours exposed to 50°C hot chlorinated solution. This indicates that chemical interaction probably occurs in the sample. Also the melting temperature of bimodal HDPE and silane crosslinked bimodal HDPE had about the same melting temperature over the exposure time within the experimental standard deviation limit.

Figure 7 shows the degree of crystallinity of bimodal HDPE and silane crosslinked bimodal HDPE after different exposure times (up to 1000 hr) at 50 and 70°C in the

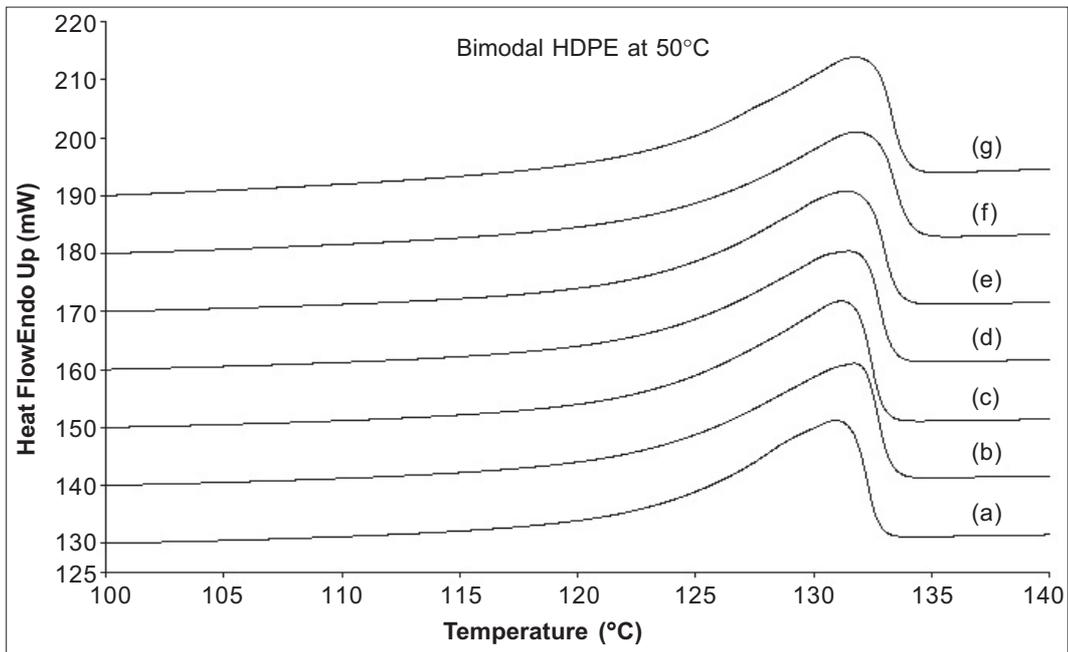


Figure 3 DSC thermograms of bimodal HDPE sample exposed to hot chlorinated solution at 50°C for different duration indicated in (a) unexposed, (b) 100 hr, (c) 200 hr, (d) 400 hr, (e) 600 hr, (f) 800 hr, (g) 1000 hr

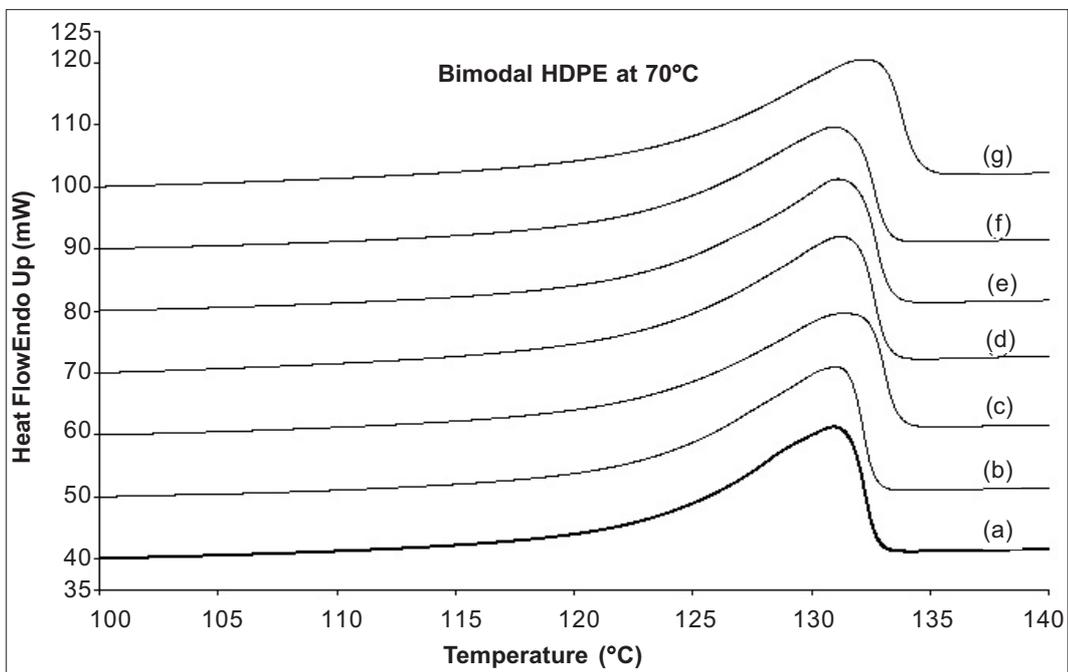


Figure 4 DSC thermograms of bimodal HDPE sample exposed to hot chlorinated solution at 70°C for different duration indicated in (a) unexposed, (b) 100 hr, (c) 200 hr, (d) 300 hr, (e) 400 hr, (f) 500 hr, (g) 600 hr

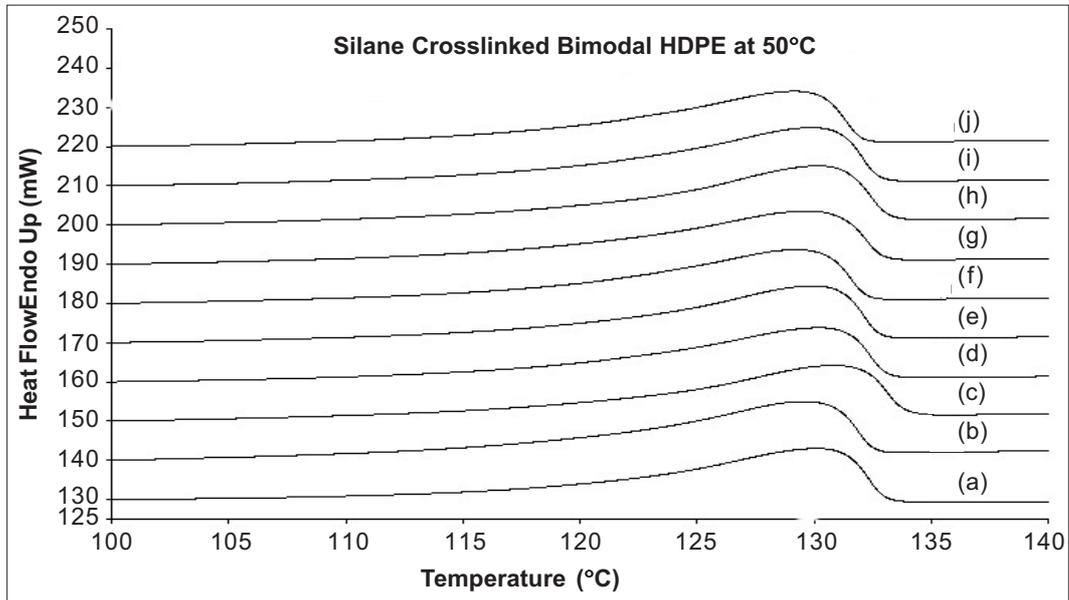


Figure 5 DSC thermograms of silane crosslinked bimodal HDPE sample exposed to hot chlorinated solution at 50°C for different duration indicated in (a) unexposed, (b) 100 hr, (c) 200 hr, (d) 300 hr, (e) 400 hr, (f) 500 hr, (g) 600 hr, (h) 700 hr, (i) 800 hr, (j) 900hr, (k) 1000 hr

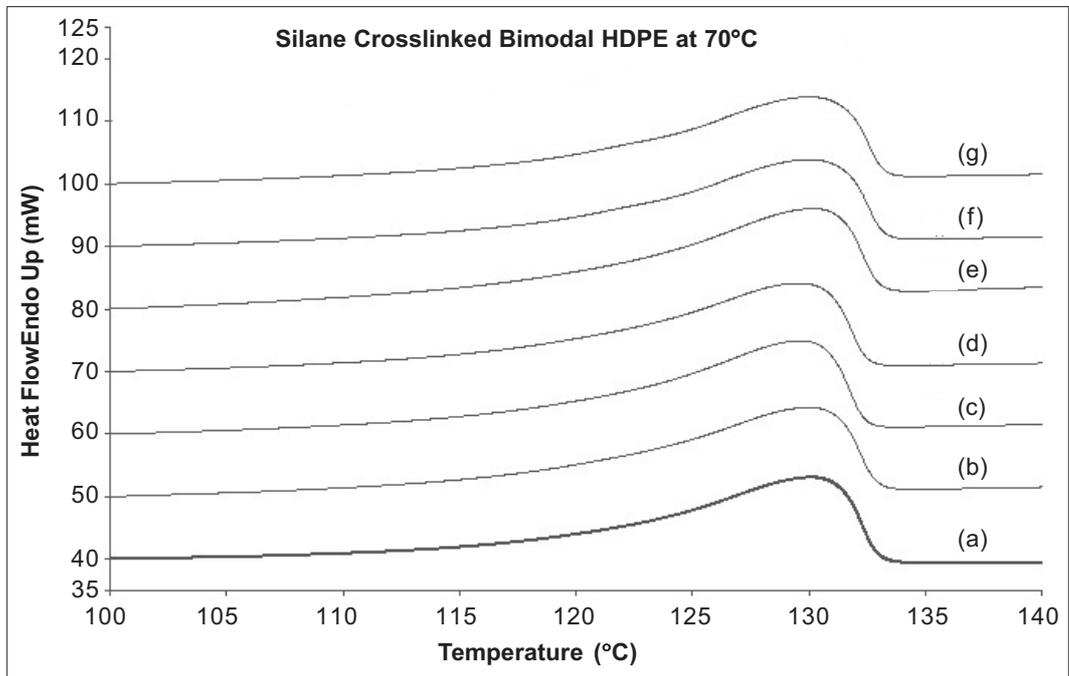
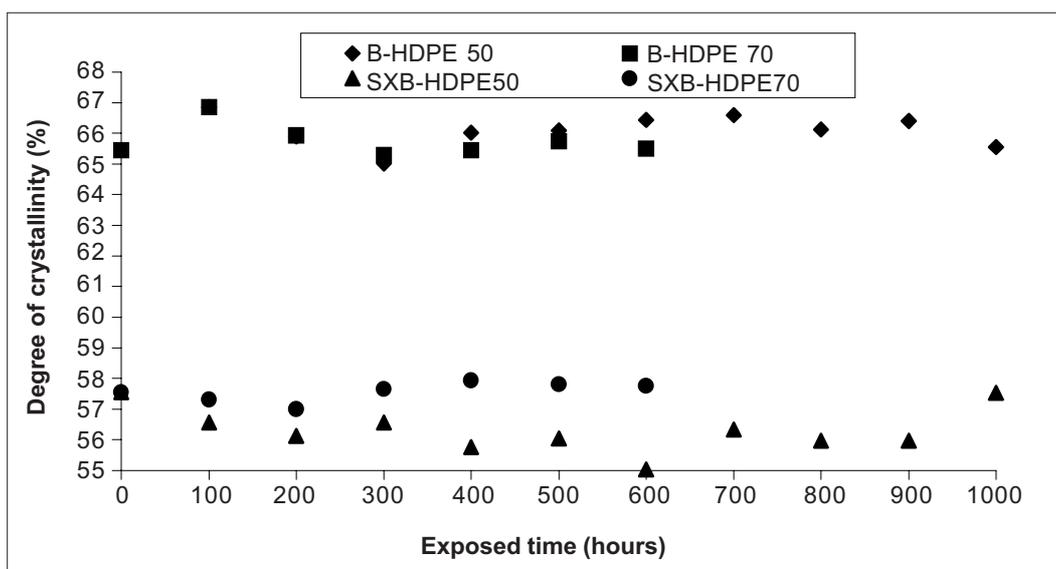


Figure 6 DSC thermograms of silane crosslinked bimodal HDPE sample exposed to hot chlorinated solution at 70°C for different duration indicated in (a) unexposure, (b) 100 hr, (c) 200 hr, (d) 300 hr, (e) 400 hr, (f) 500 hr, (g) 600 hr

Table 3 Melting temperature of bimodal HDPE and silane crosslinked bimodal HDPE before and after exposure to hot chlorinated solution.

Material	B-HDPE		SXB-HDPE	
	50	70	50	70
Exposure Temperature °C	50	70	50	70
Exposure Times (hours)	T_m	T_m	T_m	T_m
0	130.93	130.93	130.13	130.13
200	131.73	131.00	130.77	129.60
400	131.17	131.20	129.93	130.13
600	131.50	132.20	129.66	130.00
800	131.80	–	129.83	–
1000	131.73	–	129.87	–

**Figure 7** Degree of crystallinity of bimodal HDPE and silane crosslinked bimodal HDPE after different exposure times at 50 and 70°C

immersion test. The results show that a slight increase of crystallinity at the beginning of the thermo-oxidative treatment, which is probably due to the annealing effect of the thermal cycle or due to secondary crystallisation processes occurring below the melting temperature. Both HDPE materials present slight increment of crystallinity compared with unexposed material.

Among these materials, bimodal HDPE shows slight increment which is about 1.96%, followed by silane crosslinked bimodal HDPE with 0.06% in crystallinity after

exposure to hot chlorinated solution at 50°C for 1000 hours. Based on the results, the increase in crystallinity is not probably due to chain scission of tie molecules traversing the amorphous regions. The chain scission allows the resulting freed segments to crystallize [14]. The creation of new intermolecular polar bonds due to carbonyl groups lead to the greatest effect on crystallinity.

Generally, the scission of the bonds happens in the amorphous regions of the polymer where the segments of the polymers are packed more loosely and can be more easily attacked by water. The broken chains could improve the mobility of the segments and allow them to be rearranged regularly. Bond breakage in silane crosslinked bimodal HDPE could probably occur at the outer surface of the polymer. This is because the degree of crystallinity shown is not significant. Therefore, surface degradation does not show much effect on the crystallinity because the mobility of the broken segment at the surface as a result of degradation probably increases the thickness of the crystallinity on the surface only. This small increase in the melting temperature of the polymers could be caused by the increase in these “perfection” of the crystallites on the polymer surfaces and the slight increase of the molecular weight of the polymer.

4.4 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Degradation due to the oxidation process as a result of exposing samples to the hot chlorinated solution at 50°C for 200, 500 and 1000 hours was detected by FTIR. Increase of the hot chlorinated solution exposure duration led to a significant increase in the carbonyl group concentration due to the higher oxidation of the molecules. The increase in the carbonyl band region (1600–1800 cm^{-1}) is a characteristic for thermal degradation. Carbonyl groups usually account for most of the oxidation products on thermo-oxidative degradation of polyethylene; the concentration of carbonyl groups can be used to monitor the progress of degradation [15]. The carbonyl absorption is composed of different overlapping bands corresponding to acids (1712 cm^{-1}), ketones (1723 cm^{-1}), aldehydes (1730 cm^{-1}) and lactones (1780 cm^{-1}).

Figures 8 to 11 show the carbonyl bands for the studied materials. The growth of carbonyl absorbance was almost negligible for all samples during the hot chlorinated solution exposure for 200 hours. Above 200 hours of exposure, bimodal HDPE and silane crosslinked bimodal HDPE showed a large increase in carbonyl region. The development of carbonyl region was very small for silane crosslinked bimodal HDPE. Other bands such as hydroxyl, vinyl, acetaldehyde and vinylidene group are not calculated because they have similar trends of growth with the hot chlorinated solution exposure times.

However, bimodal HDPE and silane crosslinked bimodal HDPE show various band presence near 3500–4000 cm^{-1} in the FTIR spectrum, which is shown in Figures 8 to 11. The bands appeared to be due to the large number of terminal –OH groups resulting from the bond scission due to the thermal degradation and the new band at 1600–1800 cm^{-1} was assigned to the carbonyl stretching vibration from the oxygenated

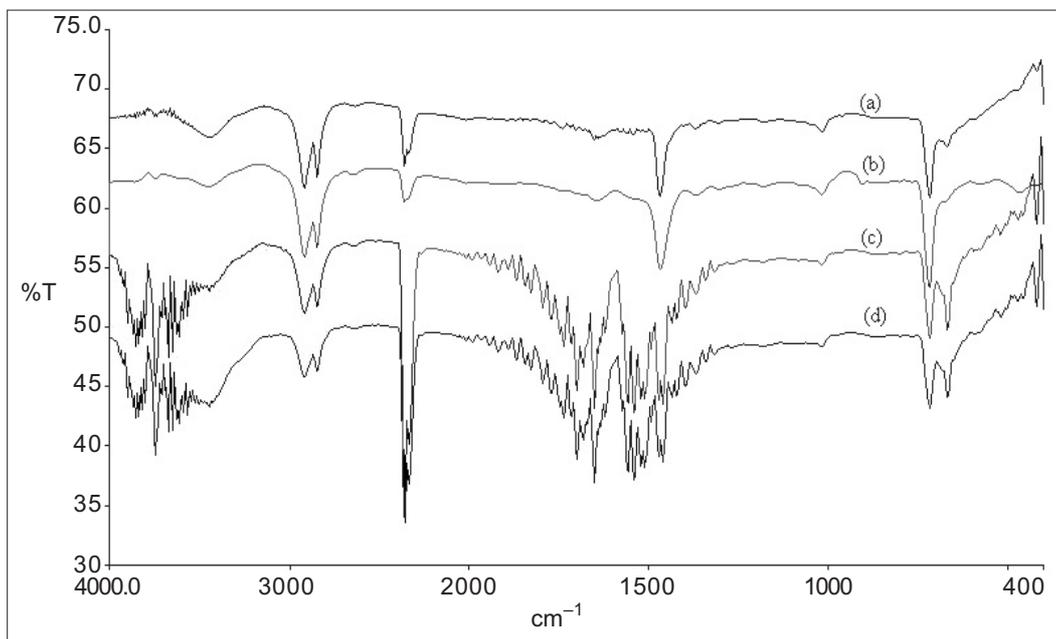


Figure 8 FTIR spectrum of bimodal HDPE before and after exposure to hot chlorinated solution at 50°C for various exposed times. (a) 0 hr (b) 200 hr (c) 500 hr and (d) 1000 hr

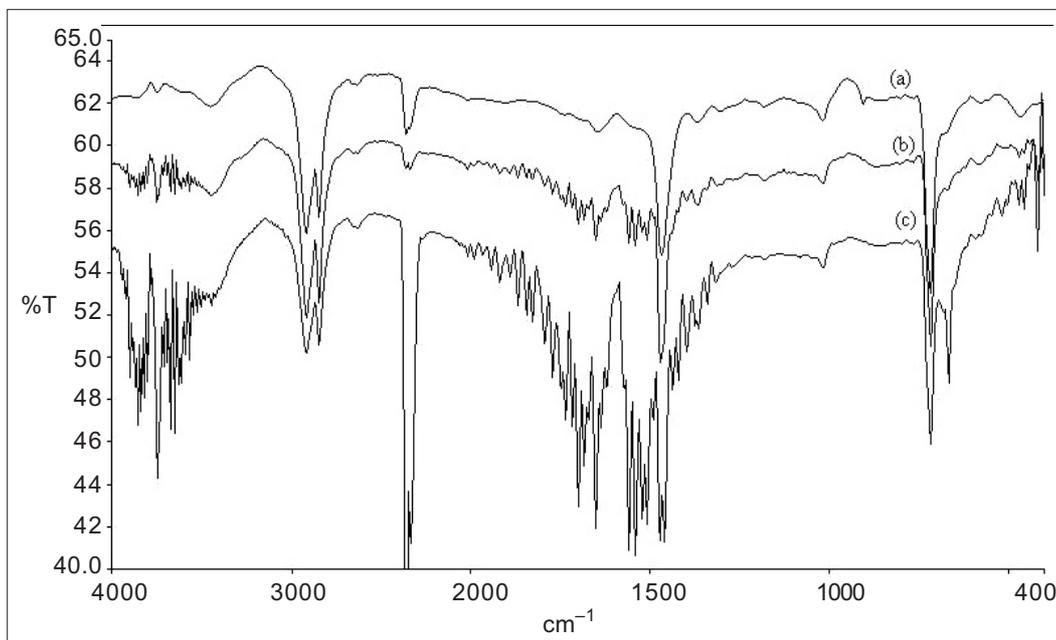


Figure 9 FTIR spectrum of bimodal HDPE before and after exposure to hot chlorinated solution at 70°C for various exposed times. (a) 0 hr (b) 300 hr and (c) 600 hr

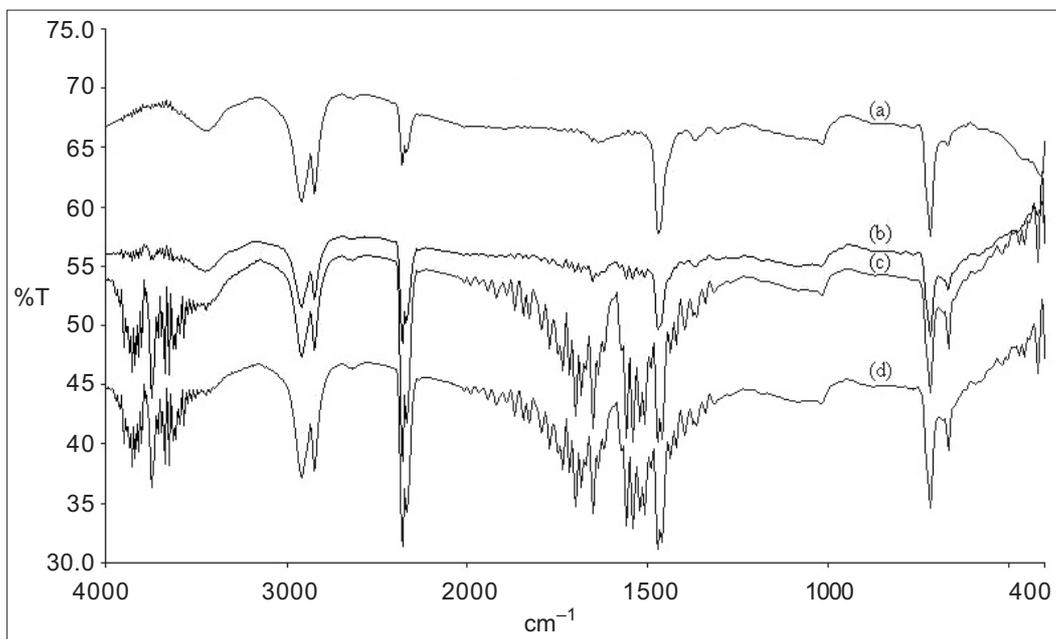


Figure 10 FTIR spectrum of silane crosslinked bimodal HDPE before and after exposure to hot chlorinated solution at 50°C for various exposed times. (a) 0 hr (b) 200 hr (c) 500 hr and (d) 1000 hr

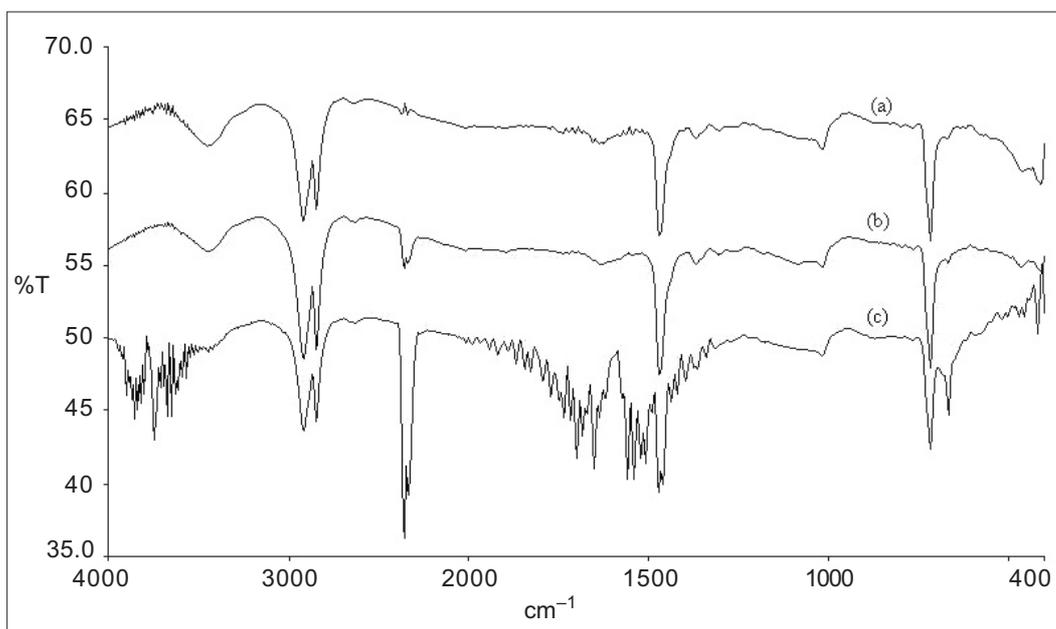


Figure 11 FTIR spectrum of silane crosslinked bimodal HDPE before and after exposure to hot chlorinated solution at 70°C for various exposed times. (a) 0 hr (b) 300 hr and (c) 600 hr

product [16]. From the analysis of FTIR spectra, it was confirmed that carbonyl group was produced during diffusion process of hot chlorination solution to HDPE over the exposed times. As shown in Figures 8 to 11, the relative oxidation level was the largest for the bimodal HDPE, followed by silane crosslinked bimodal HDPE. This proved that thermal oxidative degradation is more difficult in crosslinked state than uncrosslinked linear chain state for bimodal HDPE.

4.5 Scanning Electron Microscopy-Microscopic Examination

In order to understand the influence of hot chlorinated solution on bimodal and silane crosslinked bimodal polyethylene, voids growth on the surface of the samples were examined by using scanning electron microscopy after 100 hours of exposure time. The SEM micrographs of sample surface are shown in Figures 12 to 13.

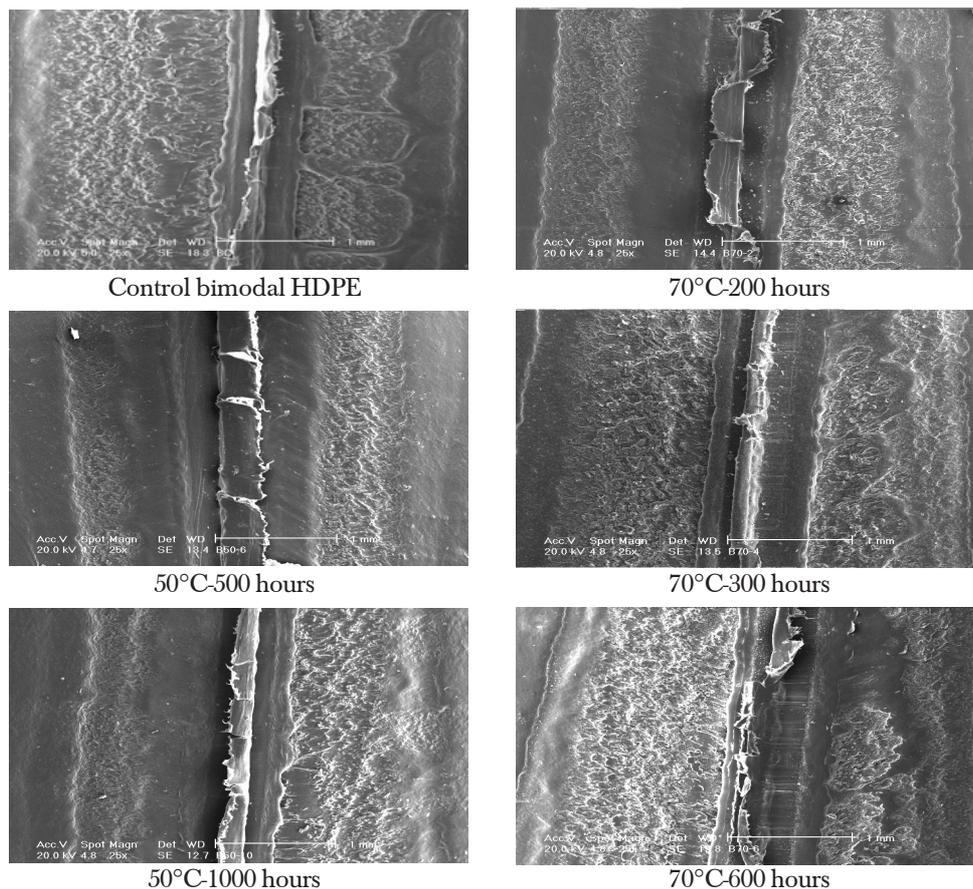


Figure 12 SEM micrographs of bimodal HDPE sample surface before and after exposure to hot chlorinated solution at 50 and 70°C for various exposure times. (Magnification 25×)

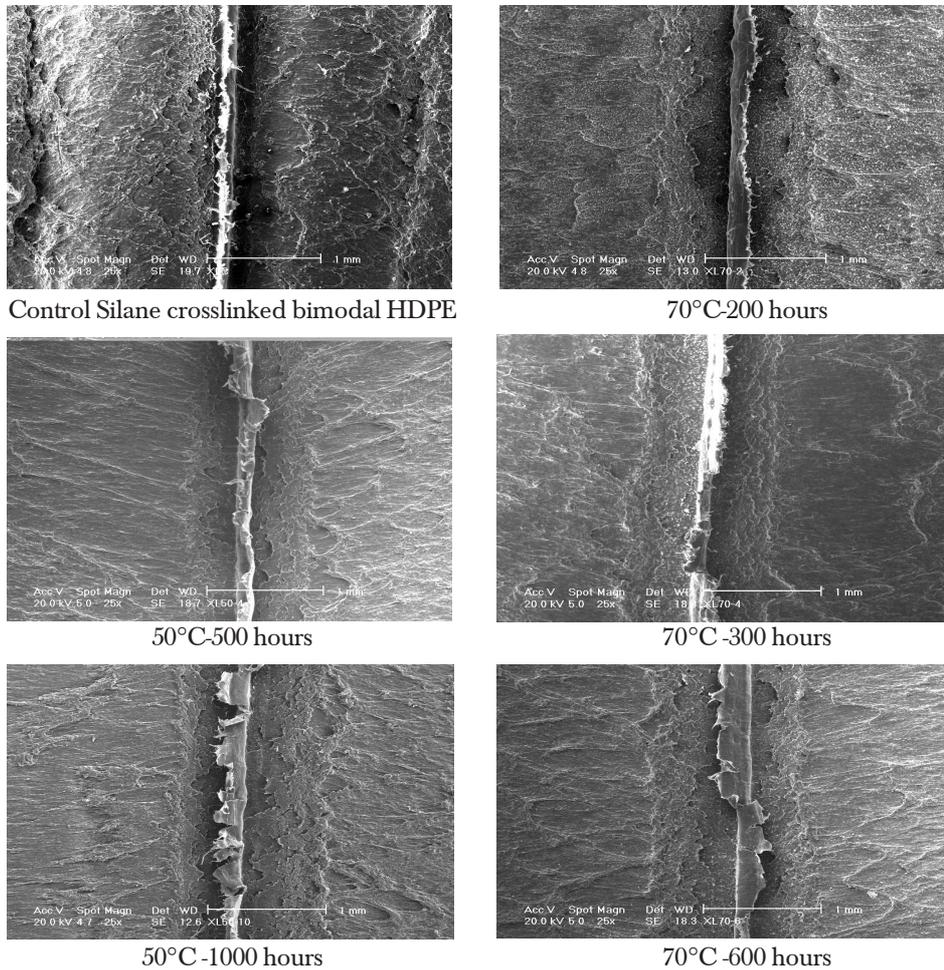


Figure 13 SEM micrographs of silane crosslinked bimodal HDPE sample surface before and after exposure to hot chlorinated solution at 50°C and 70°C for various exposure times. (Magnification 25×)

The SEM micrographs of the bimodal and silane crosslinked bimodal HDPE may relate to the changes in the mechanical and thermal properties. Scanning electron microscopy examination focus on Boston rounds bottles in the lower chime area near the parting line. This area is where the tangential and radial stresses are constrained by the bottom of the bottle. This is because the ends of the parison pinch-off concentrate the stress. The crack is most likely to form and remain near the parting line, rather than at any other area around the circumference of the lower chime.

The SEM micrographs in Figures 12 to 13, illustrate that the parting line of the three HDPE bottle was still coherent and there were no fracture failure on the parting line surface. With SEM cross-section examination, it was confirmed that after 1000 hours of hot chlorinated solution exposure, the parting line surface was still intact and there

was no obvious degradation observed (discoloration), surface void and macro void formation. Surface void and macro void may probably occur after longer hours of exposure. The SEM micrographs suggest that the two-sample HDPE material after exposure did not show any obvious micro cracks.

5.0 CONCLUSIONS

From the analysis, the following conclusions can be drawn for the first 1000 hours of the study; Bimodal HDPE and silane crosslinked bimodal HDPE has slightly deteriorated due to hot chlorinated solution exposure as it was concluded from tensile, impact, DSC and FTIR results. This deterioration did not occur microscopically, which was not easily detectable with mechanical and physical appearance. No significant reduction in transmissivity values were observed in bimodal and silane crosslinked bimodal HDPE in exposure at 70°C. The bottle when exposed to hot chlorinated solution at 50 and 70°C with exposure times up to 1000 hr did not show any significant difference in the physic-mechanical behavior. B-HDPE and SXB-HDPE have good oxidative resistance against hot chlorinated solution at 70°C.

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