ENVIROMENTAL STRESS CRACK RESISTANCE (ESCR) ANALYSIS OF BLOW MOULDED HIGH DENSITY POLYETHYLENE (HDPE) CONTAINERS EXPOSED TO SURFACE ACTIVE AGENTS (PANOX 19)

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Abstract

ESCR properties of unimodal, bimodal and silane crosslinked bimodal HDPE were investigated as a function of PANOX 19 (polyoxyethylated nonylphenol ether), exposure times in range of 0 - 1080 hours at 80 °C in an accordance to the ASTM D2561-95 procedure B. Degradation changes in the three HDPE materials were monitored by ultimate tensile strength, ultimate strain, drop impact test and characterized by DSC, FTIR and SEM. The mechanical properties occurred most rapidly starting at 120 hours duration. This unusual phenomenon was corroborated by chemical measurements (crystalinity and melting temperature). Meanwhile SEM was used to examine surface cracking. From the results, unimodal HDPE shows the best resistance towards the surface-active agent (SAA). Meanwhile bimodal HDPE shows the worst resistance towards the surface-active agent. Both mechanical and chemical analysis indicates that the oxidative degradation process is confined to the exposed surface of the samples. The three HDPE did not fail in the reasonable time under bottle stress crack (BSC) test conditions, but under drop impact test, a brittle failure mechanism was observed on bimodal HDPE and silane crosslinked HDPE. Blow molded HDPE that exhibit a brittle mode at 360 hours is the bimodal HDPE and 480 hours for silane crosslinked bimodal HDPE, which caused the body of the bottles form cracks.

KEYWORKS: ESCR, Surface Active Agent, HDPE, DSC, FTIR and SEM.

INTRODUCTION

Polyethylene, which is used as packaging for many household and industrial chemicals, must display excellent environmental stress crack resistance (ESCR). A variety of tests exist to check the ESCR of polyethylene. Choosing which of these ESCR methods is most applicable to the specific application for which the resin is intended is up to the discretion of the engineer. The most common bottle test methods include the bottle stress crack (BSC) tests, the top load stress crack (TLESCR) test, and the internal pressure (IP) test [1].

High-density polyethylene (HDPE) fails at a significantly lower time in creep tests when it is in contact with surface-active agents, such as detergents, although it has a considerably longer time to creep failure when it is exposed only to the air. It is believed that this phenomenon is the creep failure caused by the diffusion of surface active agents to the intercrystalline regions of HDPE and it is called environment stress cracking (ESC), which is distinguished from the failure caused by swelling with organic solvents such as benzene or xylene. The time to creep failure by a surface-active agent is called environment stress cracking resistance (ESCR)[2].

Based on the ESC studies of HDPE [2,3,4,5], it is generally believed that ESC occurs via the processes illustrated in Fig. 1. Namely, formation of micro voids (< 1μm) in intercrystalline regions just after loading [Fig. 1 (a)]. Formation and subsequent growth of macro voids caused by the weakening in cohesion between molecular chains in intervoids with the action of a surface active agent [Fig.1 (b)], and formation of crazes which are composed of interconnected voids and fibrils [Fig 1. (c)]. The process from (a) to (c) is a void growth process. Growth of the crazes caused by the breakdown of tie molecules in the fibrils [Fig.1 (c), where tie molecular join the crystalline lamellae to support the applied stress]. The process from (c) to (d) is a craze growth process. Finally, a crack starts at the tip of the craze, leading to brittle failure [Fig 1 (e), (f)].

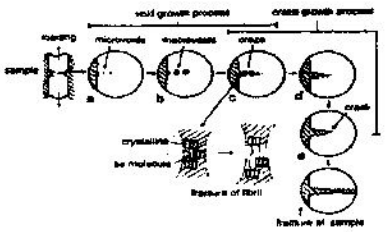


Figure1. Schematic illustration of environment stress cracking.

It has been reported that the ESCR of HDPE increases with increasing molecular weight [6], density of branches on the polymer chain, [7] and decreasing percentage of low molecular weight hydrocarbons [8]. Among these factors, the increase in the molecular weight of the HDPE is the most effective for the improvement of ESCR, since the ESCR increases with increasing number of tie molecules [9] which are effectively formed by species with molecular weight greater than 10^5.However, an increase in the molecular weight of the polymers tends to lead to a decrease in its melt flow and is unfavorable for its process ability. According to the model for the formation of the tie molecules proposed by Huang and Brown [10], the probability of forming the tie molecules is only about 0.02 for molecules of molecular weight 10^5 but it will increase remarkably and reach more than 0.30 when the molecular weight of the molecules becomes greater than 10^6. Therefore, it can be assumed that with modification of macromolecular with silane crosslinked on a conventional HDPE will lead to a larger number of tie molecules and concomitantly a longer ESCR with only a small decrease in melt flow properties.

The purpose of this study is to investigate the effect of surface-active agent in three different type of HDPE on ESCR, which has different chemistry contents. This study details the effect of HDPE type on the BSC bottle test. Bottle failure mechanisms are also discussed.

2. EXPERIMENTAL

2.1 Bottles Preparation

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

Table 1. Specifications for the HDPE resins

Description	Producer /Trade Name
Umimodal HDPE, Density -0.954 g/cm^3, MI-0.25 g/10min	Polyethylene (M) Sdn Bhd / Etilinas HD5403AA
Bimodal HDPE, Density -0.956 g/cm^3, MI-0.35 g/10min	Titan Polyethylene (M) Sdn Bhd/ Titanzex
Silane Crosslinkable bimodal HDPE, Density -0.956 g/cm^3, MI-0.35 g/10min	Polymer Engineering Research group. UTM

2.2 Preparation of Environment Stress Cracking Test In Bottles.

The BSC test was conducted by filling the bottles to one third-capacity with 100% concentrate PANOX 19 (polyoxyethylated nonylphenol ether) with an alcohol based surface-active agent. The filled bottles were then capped and placed on tray in an oil bath (Memmert Co, Model WB/OB 10) at 80°C. Daily visual inspections were used to monitor the bottles for failures. The outside of the bottles was exposed to the surface-active agent .The ESCR of the bottle samples was defined as the time at which the solution in the bottles leaks out on to the tray caused by the environment stress cracking of the bottle. The interval time used is 120 hours. This testing was carried out in accordance to the ASTM D2561-95 procedure B [11].

3.0 TESTING AND ANALYSIS

Four polymer characterization techniques, density, differential scanning calorimetry (DSC), fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were used to compare the surface active agent treated samples to the non-surface active agent treated sample. The main purpose of these techniques was to characterize, qualitatively and quantitatively the variation of both samples.

3.1 Mechanical Testing

Tensile test was performed according to ASTM D638-Type IV [12] 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 surface-active agent 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 [13].

3.3 Density Measurement

Density measurements of the sample before ESCR and after ESCR were obtained using a Techne® density gradient column, model DC-4 gradient column. A one-meter long glass gradient tube is filled with solution consisting of a mixture of isopropanol and water at 23 °C which give a density range of 0.93-0.960 g/cm^3 following the procedures described in ASTM standard 1505-98 [14]. Eight glass density floats were used to calibrate the column, which was maintained at the temperature of 23 ±1°C during measurement.

3.4 Differential Scanning Calorimetry (DSC) Analysis

Samples were characterized 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°C min^{-1} in two runs in accordance to ASTM D3417-99 [15]. 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 (Tm), 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 Hm = 290 J/g [16].

3.5 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier Transform Infrared (FTIR) Spectroscopy was used to qualitatively demonstrate the chemical degradation reactions of the surface-active agent on the samples by the occurrence of specific functional groups. Chemical degradation reactions of HDPE sample were characterized by using Perkin Elmer Spectrum 2000 Explorer FT-IR Spectrometer at a constant spectral resolution of R=0.5cm^{-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, silane crosslinked bimodal HDPE and unimodal HDPE due to the surface-active agent can be accurately detected by FTIR. All oxidized samples were characterized by the formation of free (non-hydrogen bonded) hydroperoxides (3550 cm^{-1}), free alcohols (3625cm^{-1}), bonded alcohols and hydroperoxides (3600-3200cm^{-1}), carbonyl (predominantly strongly overlapped ketones and carboxylic acids, ~1718 cm^{-1}), γ-Lactones (1770 cm^{-1}) and trans-vinylene bonds (966 cm^{-1})[17].

3.6 Scanning Electron Microscopy

Surface 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 ESCR tests. The number of voids and crack observed on the tested samples surface were automatically determined from the SEM photographs.

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 surface-active agent exposure time. The mechanical properties of non surface active agent treated and with surface active agent exposure of three HDPE are presented in Fig. 2 and Fig.3

Fig.2 illustrate that the elongation at break decreases drastically with surface-active agent exposure time. After 1080 hours, the strain of bimodal HDPE is reduced from 2731.60% to 768.77% (i.e. relative decrease of 71.86 %), follow by silane crosslinked bimodal HDPE, from 1076.3 % to 620.33%. Finally, Unimodal HDPE reduced from 2601.67% to 1655.90% .It should be emphasized that the decrease is really notable after 48 hours.

Fig.3 shows the variation of ultimate tensile strength with surface-active agent exposure time. Up to 1080 hours of surface active agent exposure time, the ultimate tensile strength of bimodal HDPE decreases from 38.69 MPa to 18.54 MPa, followed by a slight decreases from 22.22 to 16.31 MPa for silane crosslinked bimodal HDPE. Unimodal HDPE showed a minor decrease from 35.42 MPa to 29.81 MPa. However, an accentuate decrease is observed between 24 and 720 hours.

The bimodal HDPE and silane crosslinked bimodal HDPE exposed to SAA showed a brittle failure, which is characterized by ultimate strength and ultimate strain. Whereas, unimodal HDPE has high ultimate strength and ultimate strain.

The three polymers had shown a degradation behavior after 1080 hours exposure to the surface-active agent, which is demoted by the low ultimate strain and ultimate strength. Bimodal HDPE and silane crosslinked bimodal HDPE showed the transition of failure from ductile mode to brittle mode when exposed to surface-active agent. From the results the order for the mechanical properties decrement is Bimodal HDPE > silane crosslinked bimodal HDPE > unimodal HDPE in with respect to the ultimate tensile strength and ultimate strain results.

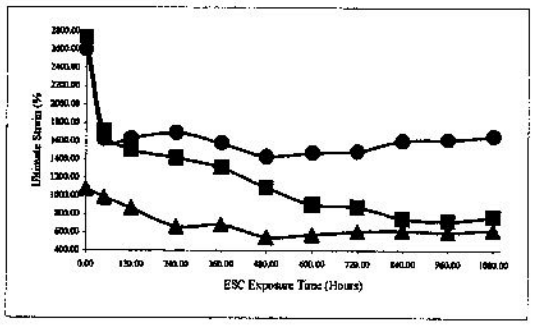


Figure 2. Variation of ultimate strain as function of surface active agent exposure time: ● Unimodal HDPE, ■Bimodal HDPE, ▲Silane crosslinked bimodal HDPE

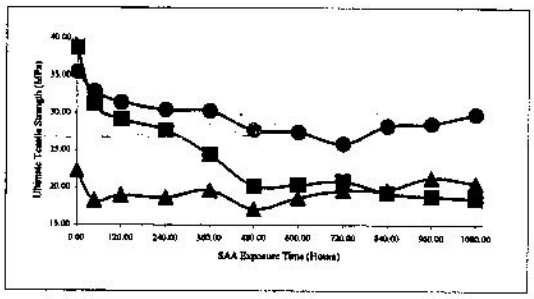


Figure 3: Variation of ultimate tensile strength as function of surface-active agent exposure time:● Unimodal HDPE,■Bimodal HDPE, ▲Silane crosslinked bimodal HDPE

4.2 Drop Impact Resistance Test

The effect of surface-active agent 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 SAA showed a decreased in impact resistance with an increased in the exposure time. Cracks from the drop impact test on the body of bimodal HDPE observed after 360 hours of exposure time, while silane crosslinked bimodal crack were observed after 480 hours of exposure. Meanwhile, no physical fracture or damage for unimodal HDPE after exposure to surface-active agent for the periods of 1080 hours. The cracking fracture of bimodal HDPE and silane crosslinked bimodal HDPE indicates that the brittleness of the bottles increases with the increasing surface-active agent exposure time. This suggests that the structure property relationship of the base polymer plays on important role to the ESCR property [18].

Table 2. Drop impact test, physical observation after various expose time.

Test Duration (hrs)	Unimodal HDPE	Bimodal HDPE	Silane crosslinked Bimodal HDPE
0	No crack	No crack	No crack
120	No crack	No crack	No crack
240	No crack	No crack	No crack
360	No crack	Crack	No crack
480	No crack	Crack	Crack
600	No crack	Crack	Crack
720	No crack	Crack	Crack
840	No crack	Crack	Crack
1080	No crack	Crack	Crack

4.3 DSC- Changes in Melting Behavior and Crystallinity

Figure 4 shows DSC melting curves of bimodal, silane crosslinked bimodal and unimodal HDPE before and after exposure for 1000 hours. The melting behavior of exposed samples is almost constant. No change in DSC curves was observed as shown in fig.4. This probably to suggest that the crystalline phase did not change with exposure time and the carbonyl group is concentrated in the amorphous regions.

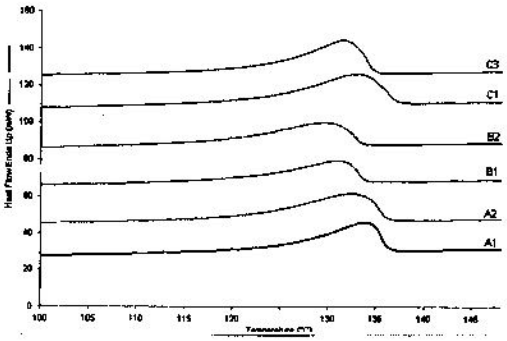


Fig.4. DSC curves of bimodal HDPE (A1, A2), silane crosslinked bimodal HDPE (B1, B2) and unimodal HDPE (C1, C3) before and after exposure for 1080 hours in surface-active agent .A1, B1 and C1 is unexposed sample.

The onset, peak and end of melting temperatures as a function of exposure time are illustrated in table 3. The unexposed bimodal HDPE has higher melting point of 133.73°C as compared to 131.50 °C after 1080 hours exposed to SAA. This indicates that chemical interaction probably occurred in the sample. The enthalpy of melting, fig.5, show a slight increment after 200 hours of exposure. This may be attributed to the slight increment in its crystallinity. This increment is thought to come from the

rearrangement of the amorphous part after chain scission by thermal degradation.

In fig.5, the data generated from the DSC are plotted as percent of melting enthalpy versus ESCR exposure time curves for each HDPE. The most obvious observation is the difference in crystalinity points. Quantitatively this difference between samples can be seen in the enthalpy change during endothermic melting. ΔHm for unexposed bimodal HDPE is 5 % lower than exposed sample with melting enthalpy of 187.55 J/g. This is an evidence of the higher degree of crystallinity in the exposed samples is shows that SAA change the chemical structure of HDPE leading to an increased in the degree of crystallinity. These results are summarized in table 3.

Table 3. Thermal properties of unimodal HDPE, bimodal HDPE, silane crosslinked bimodal HDPE before and after exposure to surface-active agent.

Sample	Uni-HDPE		Bi-HDPE		XBi-HDPE	
Times (h)	0	1000	0	1000	0	1000
ρ	0.954	0.955	0.956	0.959	0.956	0.954
T_{onset}	125.33	120.53	126.29	122.69	120.09	117.43
T_m	133.80	132.33	133.73	131.50	130.90	129.50
T_{endset}	136.35	136.11	136.22	134.77	133.86	133.58
ΔHm	186.45	186.60	187.55	196.90	161.60	165.71
Cryst %	64.29	64.35	64.67	67.90	55.72	57.14

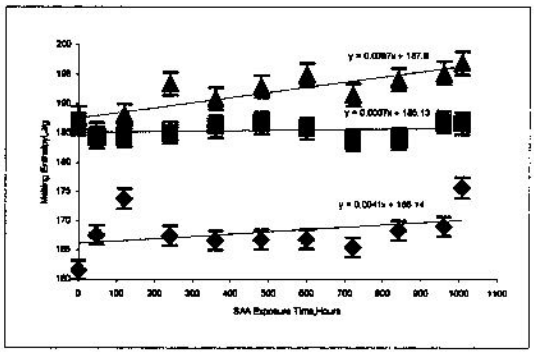


Figure 5. Melting enthalpy of unexposed bottle and surface-active agent exposure bottle over exposure time. ▲Bimodal HDPE, ■Unimodal HDPE, ◆ Silane Crosslinked Bimodal HDPE HDPE.

Among these materials, bimodal HDPE has the highest increment which is about 5%, followed by silane crosslinked bimodal HDPE with 0.09 % and finally unimodal with an increment of 2.54% in crystallinity. The increased in crystallinity is probably due to chain scission of tie molecules traversing the amorphous regions. The chain scission allows the resulting freed segments to crystallize [19]. The creation of new intermolecular polar bonds, due to carbonyl groups may also lead to this effect .The crystals become thinner after surface active agent exposure step, which was confirmed by the lower melting temperature of the sample [20]. The annealing effect at the oxidation temperature may also contribute to the increased in the crystallinity. The crystallinity differences in those three bottles examined herein suggest that the samples increment in its crystallinity is proportional to the reduced impact resistance. The increased in crystallinity is attributed to the increased in density. This is agreeable with the density results as shown in table 3.

Thermal analysis showed higher ESCR stability for unimodal HDPE compared to silane crosslinked bimodal HDPE and bimodal HDPE. Bimodal HDPE was found to be the unstable of the three high-density polyethylenes, through DSC thermal analysis results.

4.4 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Degradation due to the oxidation process as a result of exposing samples to the SAA at 80°C for 120, 720 and 1000 hours was accurately detected by FTIR. Increase of the surface-active agent exposure duration led to a significant increase in the carbonyl group concentration due to the higher oxidation of the molecule. The increase in the carbonyl band region (1600–1800cm^{-1}) is a characteristic for thermal degradation of the after exposure to SAA [21], [22]. 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 [23]. 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}).

Fig.6-8 shows the carbonyl bands for the studied materials. The growth of carbonyl absorbance was almost negligible for all samples during the SAA exposure for 120 hours. Above 120 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 unimodal HDPE. Other band such as hydroxyl, vinyl, acetaldehyde and vinylidenne group is not calculated because they have similar trends of growth with the SAA exposure times.

However, HDPE shows various band presences near 3500-4000 cm^{-1} in the FTIR spectrum, which is show in fig.6, 7 and 8. 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 product [21]. From the analysis of FTIR spectra, it was confirmed that carbonyl

group was produced during diffusion process of SAA to HDPE over the exposed times. As shown Fig 6-8, the relative oxidation level was the largest for the bimodal HDPE, follow 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.

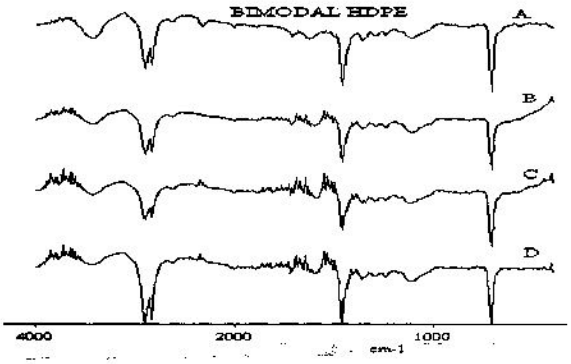


Figure 6. FTIR spectrum of bimodal HDPE before and after SAA exposure at 80 °C for duration 0 (A), 120 (B), 720 (C) and 1080 hours (D).

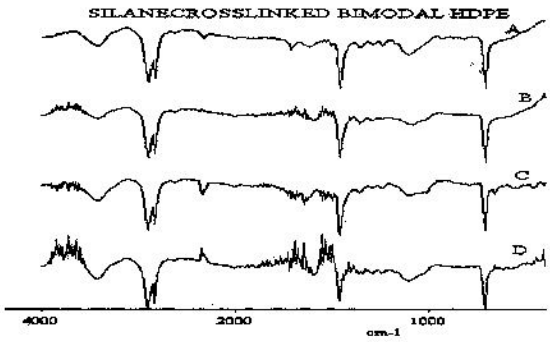


Figure 7. FTIR spectrum of silane crosslinked bimodal HDPE before and after SAA exposure at 80 °C at 80 °C for duration 0 (A), 120 (B), 720 (C) and 1080 hours (D).

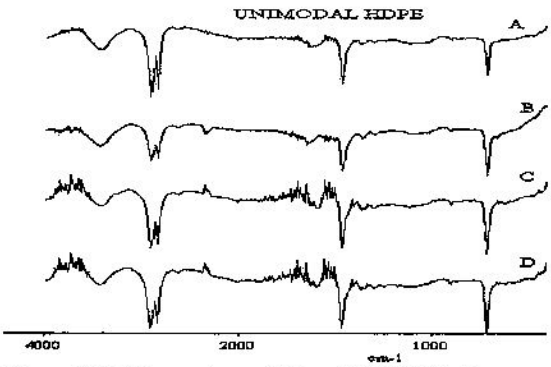


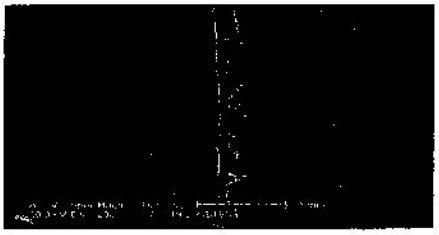
Figure 8. FTIR spectrum of bimodal HDPE before and after SAA exposure at 80 °C for duration 0 (A), 120 (B), 720 (C) and 1080 hours (D).

4.5 Scanning Electron Microscopy-Microscopic Examination

In order to understand the influence of SAA on bimodal, unimodal and silane crosslinked bimodal polyethylene, voids growth on the surface of the samples were examined by using scanning electron microscopy after 120 hours of exposure time. The SEM photographs of sample surface are shown in Fig.9 to Fig.11.

The SEM photographs of the unimodal, 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 photographs in fig 9-11 show the parting line of the three HDPE bottle was still coherent, there were no brittle failure on the parting line surface. With SEM cross-section examination, it was confirmed that after 1080 hours SAA exposure, the parting line surface was still intact and there was no obvious degradation observed (discolor) and macro void formation. In contrast, SAA exposure at 1080 hour did not cause any surface voids and crack fracture to the parting line of the bottle. This shows that no physical cracks occurring although chemical degradation do occur in the samples after 1080 hours of exposure. Physical crack may probably occur of longer hours of exposure. Physically the bottles resist cracking up to 1080 hours of SAA exposure time.



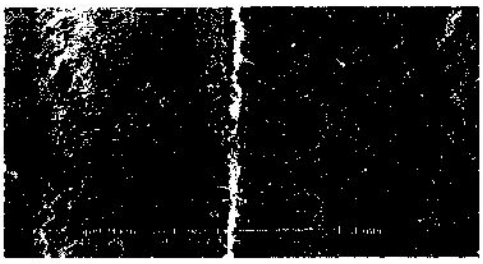
(a)

(b)

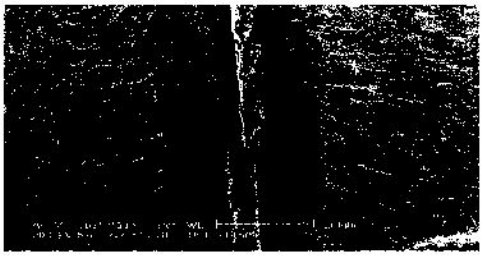
(c)

(d)

Figure 9. SEM photographs of bimodal HDPE sample surface (a) before ESCR test, (b) after ESCR tests at 80 °C for 120h, (c) after ESCR tests at 80 °C for 720h, (d) after ESCR tests at 80 °C for 1000h.



(a)



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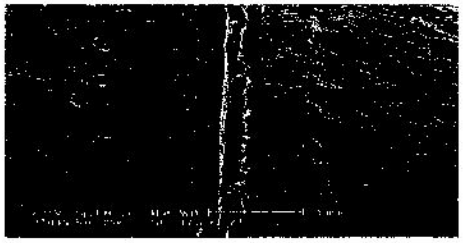

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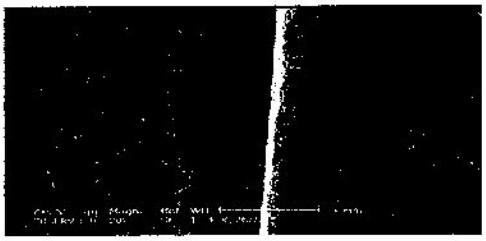
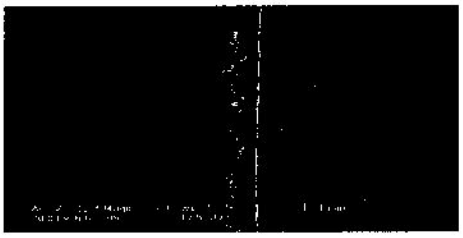


(d)

Figure 10. SEM photographs of silane crosslinked bimodal HDPE sample surface (a) before ESCR test, (b) after ESCR tests at 80 °C for 120h, (c) after ESCR tests at 80°C for 720h, (d) after ESCR tests at 80°C for 1000h.

(a)

(b)



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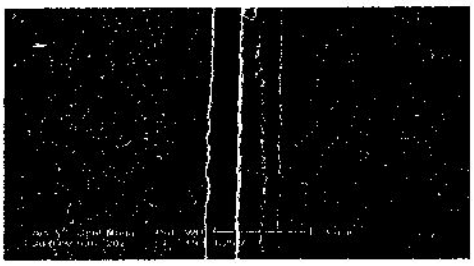

(d)

Figure 11. SEM photographs of unimodal HDPE sample surface (a) before ESCR test, (b) after ESCR tests at 80 °C for 120h, (c) after ESCR tests at 80 °C for 720h, (d) after ESCR tests at 80 °C for 1000h.

CONCLUSIONS

ESCR property of unimodal and bimodal HDPE were investigated for the purpose of developing crosslinked HDPE as an engineering material. The series of performance tests showed that unimodal HDPE has excellent ESCR property and thermal stability during the SAA exposure and was not susceptible to the thermal oxidative degradation compared to the bimodal HDPE. Therfore, it is concluded that unimodal HDPE which is crosslinked by silane method will further improved the ESCR performance.

This suggests that the structure properties are responsible for initiating the auto-oxidation of the HDPE matrix. ESCR decreases with increasing melt index and crystallinity. The incorporation of surface-active agent (polyoxyethylated nonylphenol ether) onto polyethylene initiates polymer degradation by producing free radicals, which react with oxygen molecular to create peroxides and hydroperoxides. The largest increase in carbonyl index was observed for the bimodal HDPE, which also correlated to the highest amount of produced degradation products. These results were confirmed by the sharp drop of ultimate strain and impact resistant determined by tensile and drop impact test.

The bottle stress crack test (BSC) also define as a quicker and more reproducible method for measuring the ESCR property of blow molded Polyethylene bottles. Increasing SAA exposure times, increase crystallinity and change the fracture behavior of the samples from brittle to ductile. Microscopy examination showed no cracks is initiated on the inner bottle wall near the intersection of the parting line and the lower chime because of SAA exposure duration was too short. But FTIR and DSC identified the chemical degradation occurring in the samples. These conclude that degradation occurs at chemical scale but major structure changes has yet to occur and so it's the micro-crack. Therefore silane crosslinked bimodal HDPE blow molded bottles can withstand high ESCR.

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