

THE EFFECT OF PETROL AND DIESEL ON HIGH DENSITY POLYETHYLENE (HDPE) AND CROSS-LINKED HDPE BOTTLES: TENSILE AND THERMAL PROPERTIES ANALYSIS

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ABSTRACT

The effect of petrol and diesel on High Density Polyethylene (HDPE) and cross-linked HDPE bottles (XLHDPE) are studied according to ISO175: 1999. The HDPE and cross-linked HDPE bottles were prepared by blow molding technique. The bottles were immersed in petrol and diesel for 1 day, 1 week, 8 weeks and 16 weeks at temperatures 23°C and 70°C. Tensile test was carried out to determine the modulus, tensile strength and elongation at break. The degradation of HDPE and cross-linked HDPE was monitored by DSC. The tensile properties results show that the rate of degradation for petrol immersion > diesel immersion and temperature 70°C > 23°C for both HDPE and XLHDPE. The cross-linked HDPE is more stable to petrol and diesel attack compared to HDPE. DSC shows that a small changes in crystallinity and melting point for both samples. The melting behavior of exposed samples is almost constant.

Keywords: HDPE, Cross-linked HDPE, Petrol, Diesel, Tensile Test, DSC

INTRODUCTION

Plastics are frequently brought into contact with liquids such as chemical products, motor fuel, lubricants, etc depend on their application. Under the action of a liquid, a plastic material may be subjected to several phenomena which may occur simultaneously. The absorption of a liquid and extraction of constituents soluble in the liquid may occur. So a chemical reaction, often resulting in a significant change in the properties of the plastic may occur.

Change of materials characteristics over time can often cause problems in long-term applications of polymers. These changes can usually be traced back to physical (creep, relaxation, crack condition) and chemical (degradation) causes. Change in material properties may affect adversely the mechanical behaviour of polymers in many cases. Damage of polymer structural elements can be caused by exceeding the critical strain state or fracture. It was proved that the different mechanical parameters show changes in the application period for most polymers. (Németh et al., 2001)

High density polyethylene (HDPE) has a melting point above 127 °C (typically about 135 °C) and latent heat of fusion is 290 J/g (BillMeyer, 1984). Degradation of HDPE produces low molecular weight products and oxygenated products, which have effect on melting point, heat of fusion and crystallinity. As degradation proceeds, the amount of the degraded products becomes larger and crystallinity of HDPE decreases, and hence the performance of the products declines.(Seong Ok Han et al, 1999)

Polymer is chemically attacked by two ways. First mechanism is through physical failure, due to the loss of the polymer particles or molecules that are carried away. For thermosetting polymer, the swelling pressure by attacking agent is so large that the internal cross-links are broken and the polymer physically breaks apart into little pieces that get swept away and no longer adhere. The second mechanism is chemical degradation, whereby the polymer is attacked by the chemical thus breaking the cross-links and lower the molecular weight. After the chemical reactions, the polymer may be no longer of used.(Robert, 2000)

The chemical attack of HDPE and cross-linked HDPE were studied by immersing in petrol and diesel. The tensile and thermal properties before and after immersion for a designated time were investigated.

EXPERIMENTAL WORK

Materials

The high density polyethylene (HDPE) used in this study is TITANEX HB6200, obtained from Titan Polyethylene (Malaysia) Sdn. Bhd. The petrol and diesel used is from Petronas petrol station.

Sample Preparation

The cross-linked HDPE is used to extrude bottles by using the Extrusion Blow Machine. During conventional extrusion blow of HDPE bottles, Vinyltriethoxysilane is added into the polyethylene. The extruded bottles then undergo a reactive grafting of silane molecule to the backbone of the high-density polyethylene (HDPE). The bottles then cured in boiled water for 8 hours so that the material can be cross-linked. After curing, the bottles are cut into sheets. The sheets are then cut into dumb-bell shape for tensile testing according to ASTM D638-Type V (ASTM D 638, 2001).

Petrol and Diesel Immersion

The samples were immersed in petrol and diesel for 1 day, 1 week, 8 weeks and 16 weeks at temperatures 23°C and 70°C. This testing was carried out in accordance to the ISO 175:1999. (ISO 175, 1999)

Tensile Testing

Tensile test is conducted to determine the tensile strength at break and elongation at break for a difference period of time and chemical liquid. Tensile strength and elongation at break was determined using a Lloyd tensile machine, Model EZ 20 with a crosshead speed of 10mm/min according to ASTM D638-01. For each immersion, 5 specimens were tested and the average was obtained. (ASTM D 638, 2001)

Thermal Analysis- Differential Scanning Calorimetry (DSC) Analysis

Samples were characterized by using Differential Scanning Calorimetry Analysis (Perkin Elmer®, Model DSC 7). Samples of 5.5-6.5 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 (ASTM D3417, 1999). The temperature range was 30-250°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 (H_m) were obtained, and the percentages of crystallinity were determined using the enthalpy of melting for high density polyethylene of 100% crystallinity $H_m = 290$ J/g (BillMeyer, 1984).

RESULTS AND DISCUSSION

Tensile Properties

Young's modulus or the modulus of elasticity (tensile modulus) is a ratio between stress applied and the strain, within the elastic range. The ratio of tensile force to elongation is useful in determining how long a plastics specimen will get under a predetermined load. A large tensile modulus would indicate that the plastics is rigid and resistance to stretch or elongation (Terry, 1979). Figure 1 shows that the Young's modulus of the cross-linked HDPE is higher than HDPE for both diesel and petrol for all duration at 23°C. Similar results were obtained for the temperature 70°C. This is because crosslinking change the properties of HDPE from elastic to stiff and tough. This toughness is associated with impact strength (Terry, 1979).

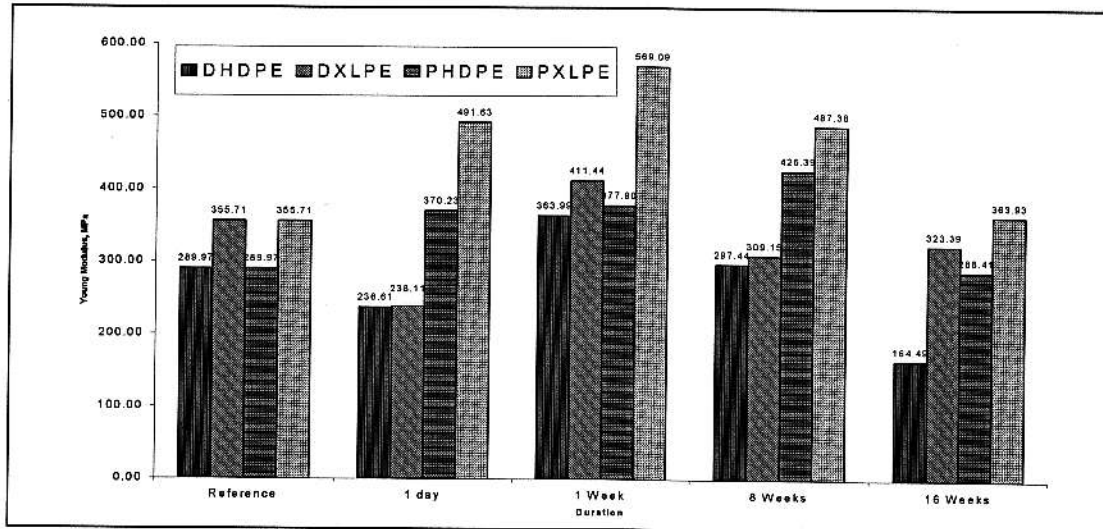


Figure 1 – Young modulus for HDPE and XLHDPE immersed in petrol and diesel at 23°C

The tensile test was carried out to determine the tensile strength at break and elongation at break as a function of exposure to petrol and diesel with respect to temperature and time. The results are presented in Figures 2 to 5.

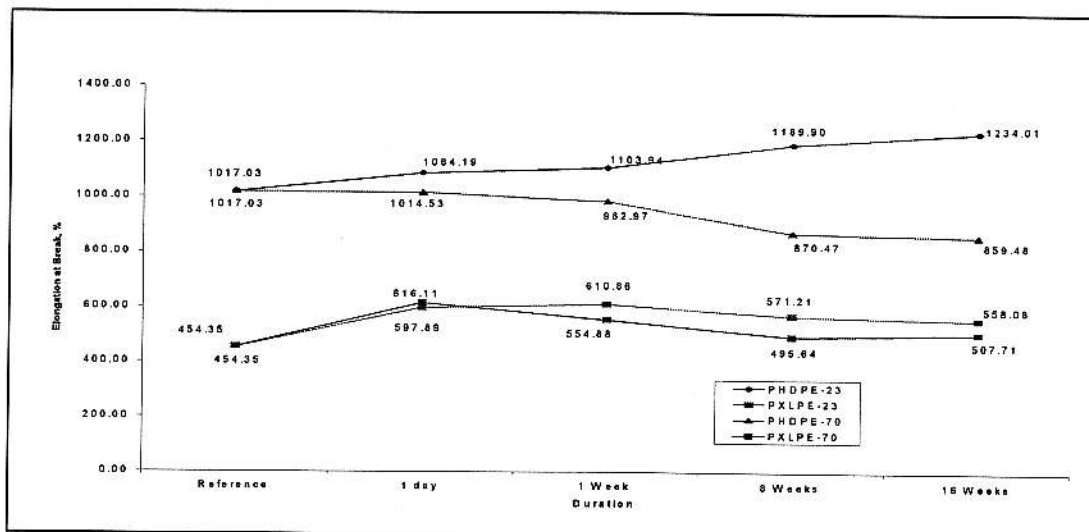


Figure 2 – Elongation at break for petrol immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

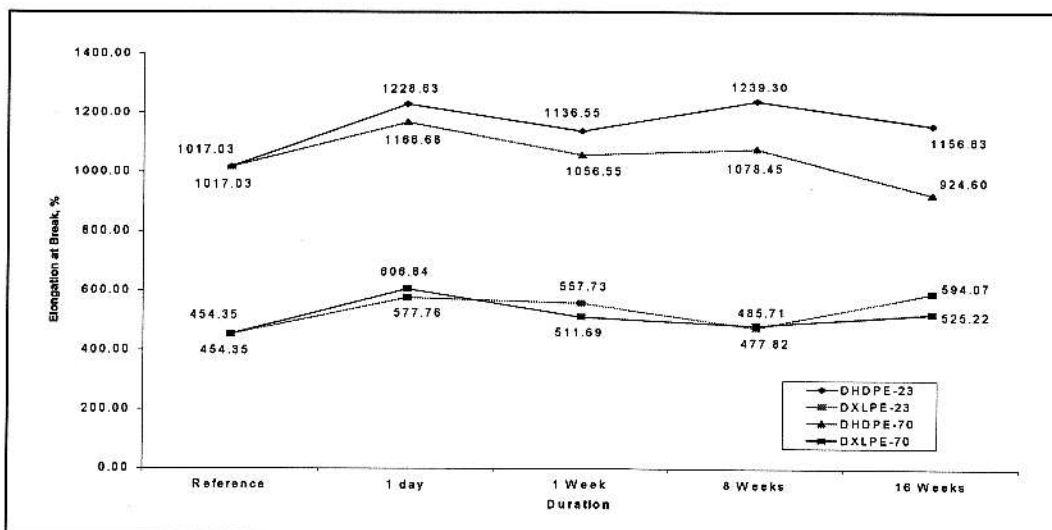


Figure 3 – Elongation at break for diesel immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

Figures 2 and 3 illustrate that the elongation at break increases slowly for HDPE in petrol and diesel at 23°C from 1017% to 1234%(petrol) and from 1017% to 1157%(diesel) while at 70°C HDPE decreases from 1017% to 859% (petrol) and from 1017% to 924% after 16 weeks. However, we can notice that the elongation at break for XLHDPE increased slowly for both petrol and diesel. Petrol increase from 454% to 558% (23°C) and 507% (70°C) whereas diesel increase from 454% to 594%(23°C) and 525(70°C) after 16 weeks.

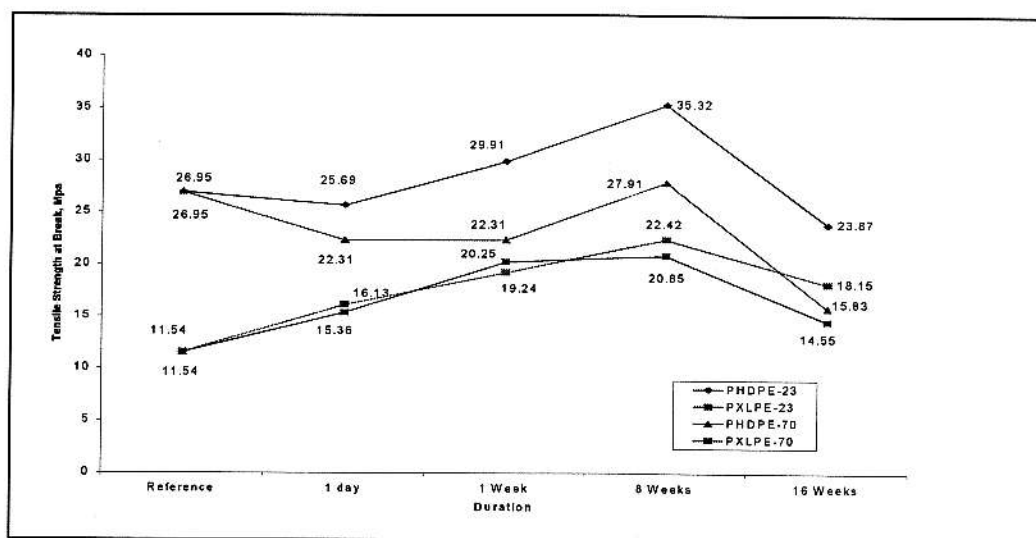


Figure 4 – Tensile strength at break for petrol immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

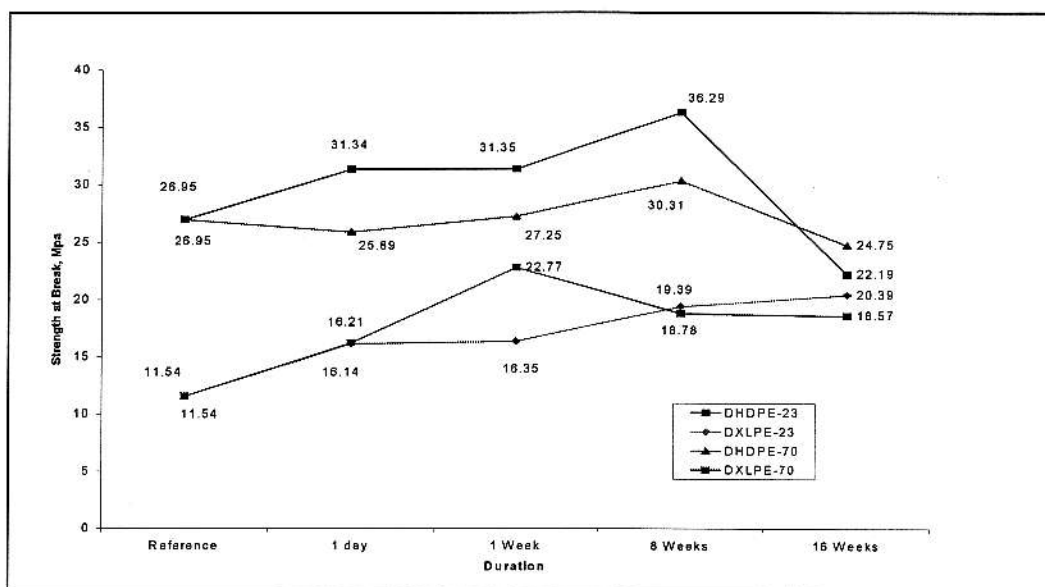


Figure 5 – Tensile strength at break for diesel immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

Figures 4 and 5 show the variation of tensile strength at break in petrol and diesel at various exposure time and temperature. For HDPE, tensile strength at break increased gradually until 8 weeks and decreased rapidly at 16 weeks for both chemicals and temperatures. Tensile strength at break decreased from 26.9MPa to 23.9MPa (23°C) and 15.8MPa (70°C) for petrol, meanwhile for diesel decreased from 26.9MPa to 22.2MPa (23°C) and 24.8MPa (70°C) at 16 weeks. However, tensile strength at break for XLHDPE increased from 11.5MPa to 18.1MPa (23°C) and 14.6MPa (70°C) for petrol and 20.4MPa (23°C) and 18.6MPa (70°C) for diesel.

The increment in the elongation at break is due to the plasticity effect as a result of petrol and diesel absorbed into the HDPE and XLHDPE. HDPE shows a steeper gradient compared to XLHDPE with time of immersion indicating the higher plasticity effect occurring in HDPE. XLHDPE resist chemical absorption which shows that crosslinking make chains more compact thus reduced the diffusion of chemicals into the chains. This will then reduced the rate of chemical degradation of the XLHDPE. In the HDPE petrol and diesel act just like a plasticizer with respect to the time of immersion. The increment in tensile strength for HDPE is probably due to the entanglement and rearrangement of chains as chemicals are being absorbed into the structure. But after 8 weeks tensile strength experience a rapid drop probably due to the destruction of the physical interactions and the weakening of the chemical bonding in the chains.

For XLHDPE tensile strength increases 8 weeks of immersion due to similar chain rearrangement and after which a drop in strength is detected, indicative of slight degradation occurring at a much slower rate. At 16 weeks of immersion XLHDPE still maintained high strength compared to HDPE in both petrol and diesel.

The HDPE and XLHDPE exposed to petrol and diesel did not exhibit brittle failure, which is characterized by yielding behavior before break. The oxidative process in both chemicals at 23°C and 70°C was demonstrated to be less severe for XLHDPE. The bottle still did not show any evidence of degradation after 16 weeks in petrol and diesel immersion tests, indicating that XLHDPE is thermally stable at the used temperature.

The results show that the tensile properties decrement is petrol immersion > diesel immersion and temperature 70°C > 23 °C with respect to the tensile strength and elongation at break. The XLHDPE is more stable to petrol and diesel attack compared to HDPE.

DSC- Changes in Melting Behavior and Crystallinity

Figures 6 to 13 shows the DSC melting curves of HDPE and XLHDPE before and after exposure for 16 weeks in petrol and diesel at 23°C and 70 °C. The melting behavior of exposed samples is almost constant. No change in DSC thermogram was observed as shown in Figure 6 to Figure 13. This probably suggests that the crystalline phase did not change with the exposure time and the carbonyl group is concentrated in the amorphous regions.

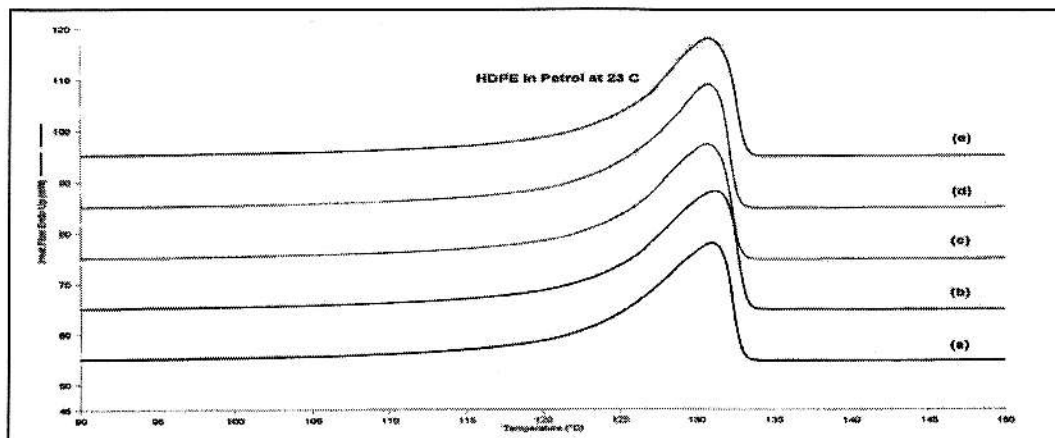


Figure 6 – DSC thermograms of HDPE sample immersed into petrol at 23°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

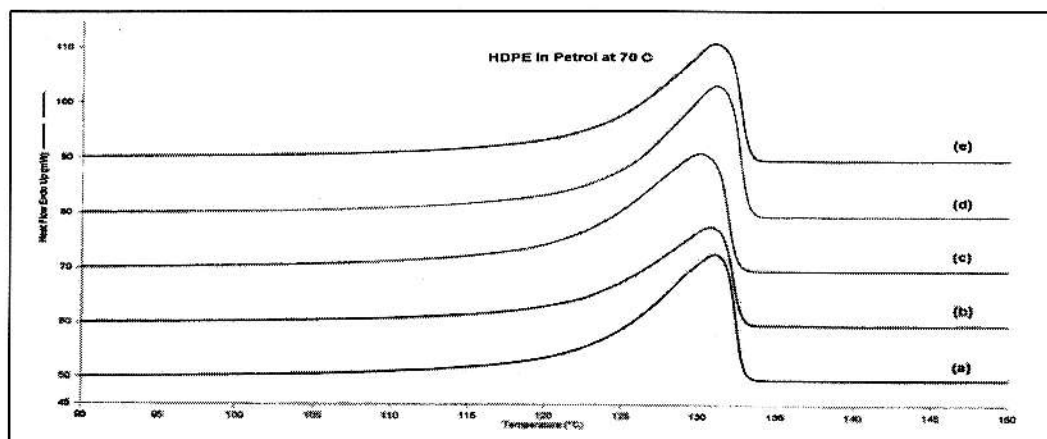


Figure 7 – DSC thermograms of HDPE sample immersed into petrol at 70°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

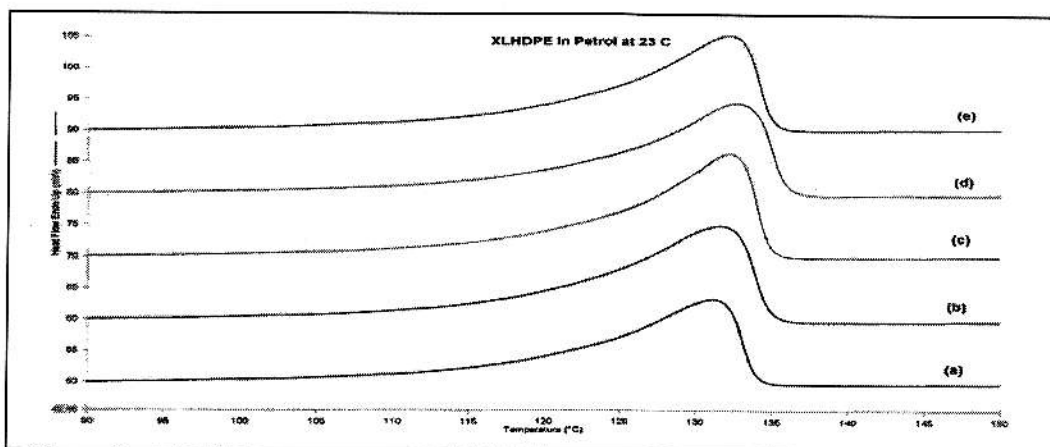


Figure 8 – DSC thermograms of XLHDPE sample immersed into petrol at 23°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

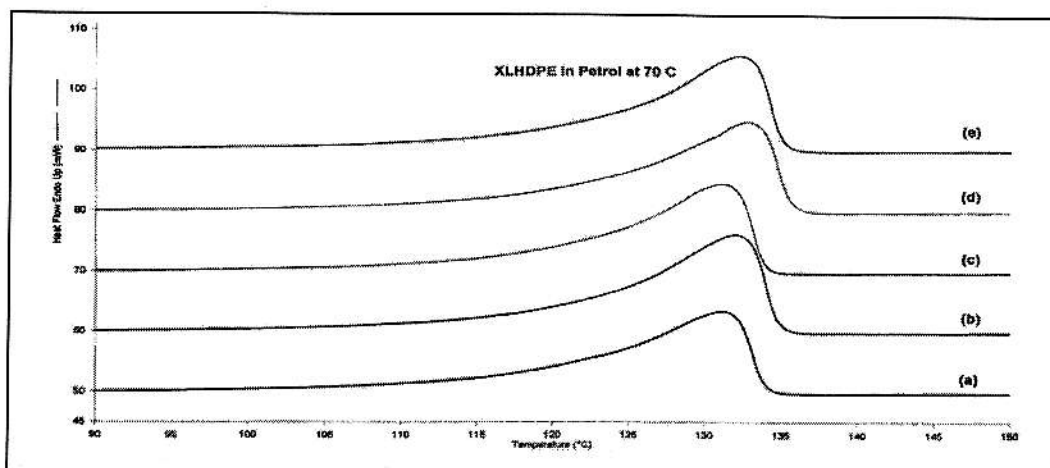


Figure 9 – DSC thermograms of XLHDPE sample immersed into petrol at 70°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

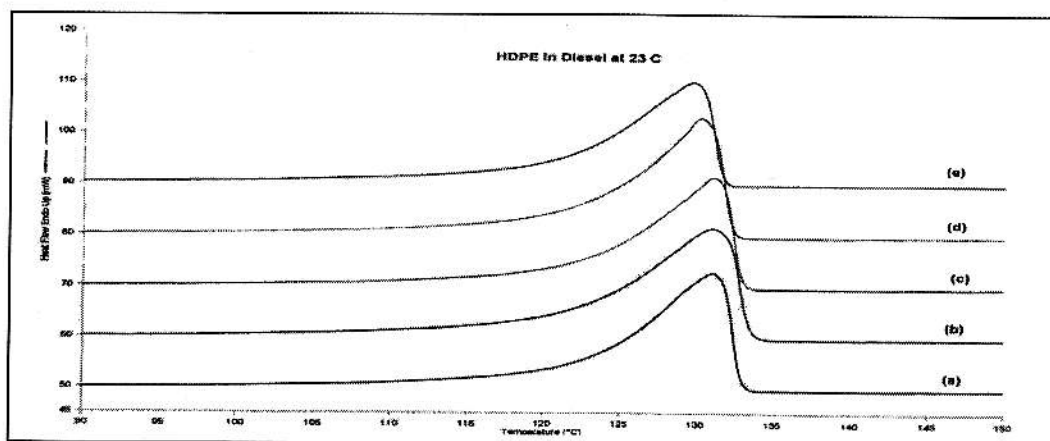


Figure 10 – DSC thermograms of HDPE sample immersed into diesel at 23°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

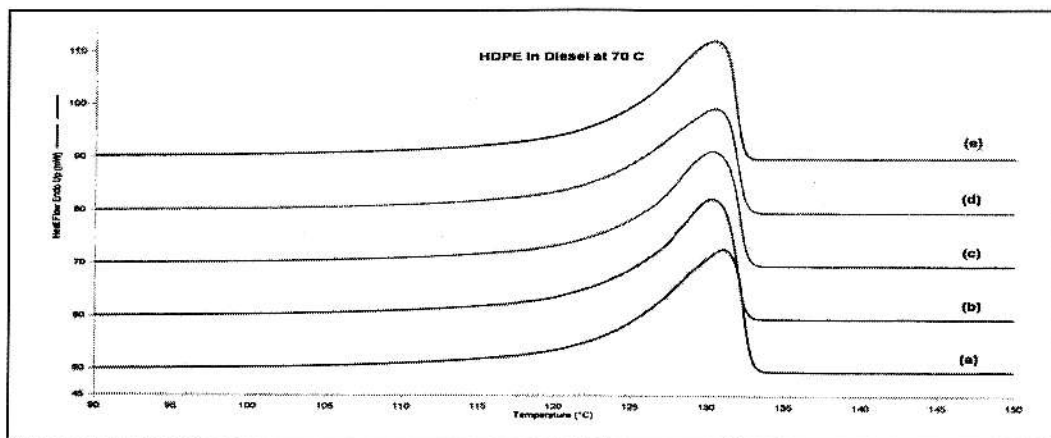


Figure 11 – DSC thermograms of HDPE sample immersed into diesel at 70°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

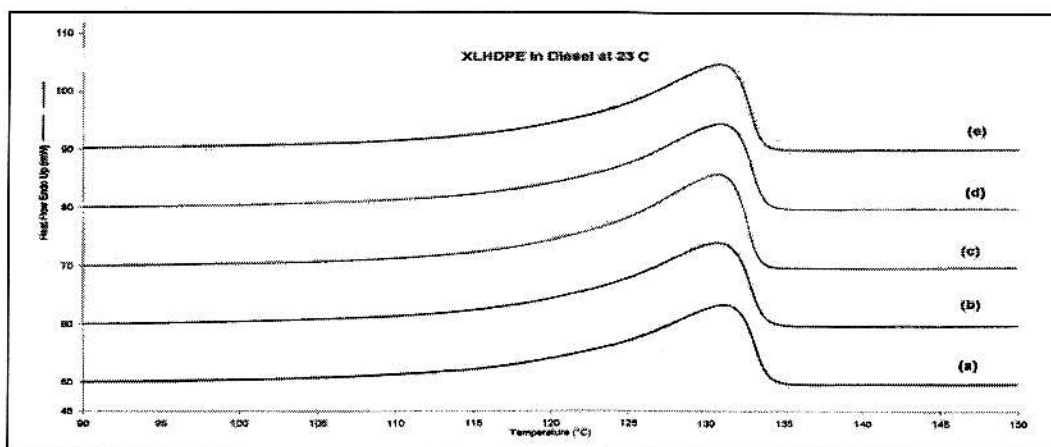


Figure 12 – DSC thermograms of XLHDPE sample immersed into diesel at 23°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

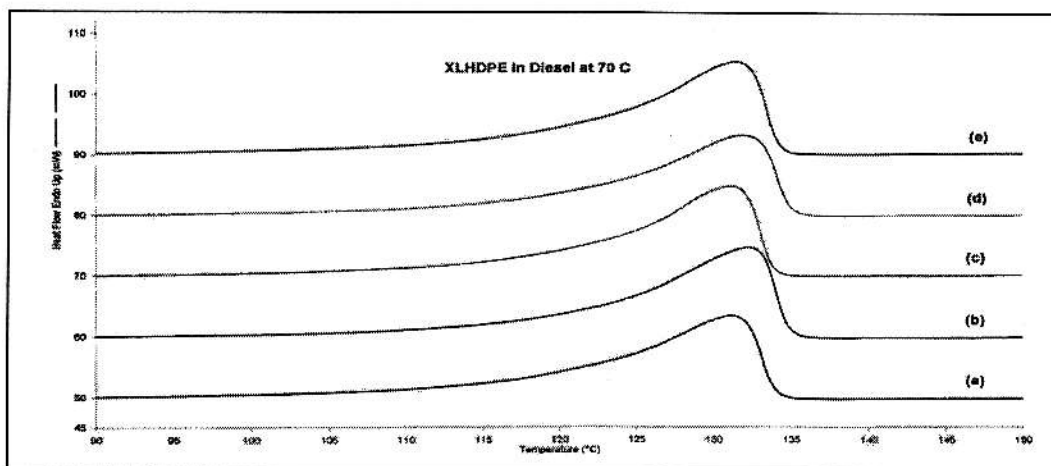


Figure 13 – DSC thermograms of HDPE sample immersed into diesel at 70°C for different duration indicated in (a) reference, (b) 1 day, (c) 1 week, (d) 8 weeks, (e) 16 weeks

The melting temperatures as a function of exposure time are illustrated in Table 1. The HDPE reference has melting point of 131.07°C as compared to 130.86°C and 130.97°C for petrol and also compared to 129.70°C and 130.43°C for diesel after 16 weeks exposed at 23°C and 70°C. The

melting temperature of XLHDPE also experience a slight change over the exposure time. This indicates that same chemical interaction probably occur in the samples.

Table 1 - Melting temperature of HDPE and silane cross-linked HDPE before and after exposure to petrol and diesel of 23 °C and 70 °C

Chemical Material	Petrol				Diesel			
	HDPE		XLHDPE		HDPE		XLHDPE	
Temperature	23°C	70°C	23°C	70°C	23°C	70°C	23°C	70°C
Times	T _m	T _m	T _m	T _m	T _m	T _m	T _m	T _m
0	131.07	131.07	131.20	131.20	131.07	131.07	131.20	131.20
1 days	131.27	131.40	131.67	132.03	131.03	130.03	130.77	132.30
1 Week	130.80	130.03	132.27	131.20	131.10	130.33	130.80	131.20
8 Weeks	130.90	131.10	132.77	132.83	130.27	130.47	131.00	132.00
16 Weeks	130.86	130.97	132.23	132.33	129.70	130.43	130.90	131.50

Figures 14 and 15 shows the degree of crystallinity of HDPE and XLHDPE after exposure times at 23 °C and 70 °C in the petrol and diesel. The results show that a slight increase in 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 crystallization processes occurring below the melting temperature. (Toh Show Chong et al, 2003) HDPE and XLHDPE shows the slight increment of crystallinity compared to unexposed material.

Among these materials, HDPE shows higher increment which is about 20.7 % and 13.7% for immersion in petrol and 8.2% and 11.4% for immersion in diesel at 23 °C and 70 °C. Silane cross-linked HDPE increased 15.8 % and 13.2% for immersion in petrol and 6.9% and 7.6% for immersion in diesel at 23 °C and 70 °C after exposure for 16 weeks. Based on the results, the increase in crystallinity is probably not due to chain scission of tie molecules traversing the amorphous regions. The chain scission allows the resulting freed segments to crystallize (Corrales et al, 2002). The creation of new intermolecular polar bonds, due to carbonyl groups lead to the greatest effect on crystallinity. (Toh Show Chong et al, 2003)

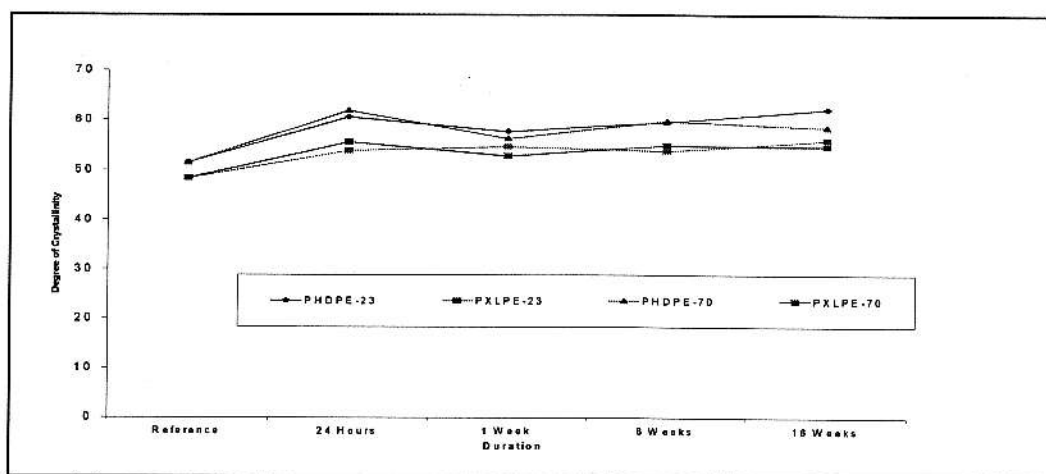


Figure 14 – Degree of crystallinity of HDPE and XLHDPE immersed in petrol at 23°C and 70°C with different time

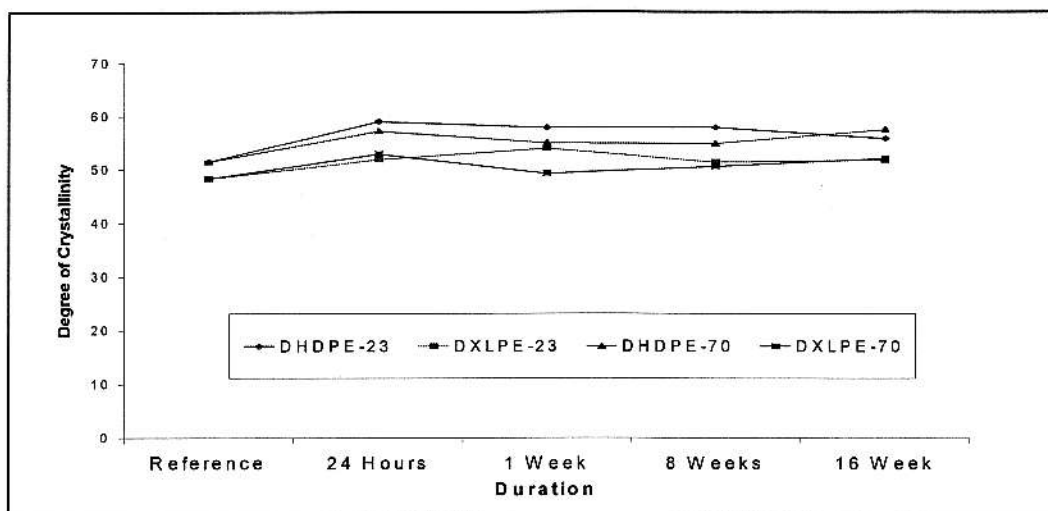


Figure 15 – Degree of crystallinity of HDPE and XLHDPE immersed in petrol at 23°C and 70°C with different time

CONCLUSION

From the analysis, the bottles when immersed into petrol and diesel at 23°C and 70°C with exposure period up to 16 weeks did not show significant difference in the tensile behavior. Both HDPE and XLHDPE show a good resistance to petrol and diesel mostly at ambient temperature, but XLHDPE show greater resistance at 70°C compared to HDPE. Young's modulus of the cross-linked HDPE higher than a HDPE show that XLHDPE more stiffness and toughness.

DSC melting thermogram generally show that the melting behavior almost is constant, suggesting that the crystalline phase did not change with the exposure time. HDPE and XLHDPE show slight increment in crystallinity compared to unexposed material. The slight changes in the melting temperature and crystallinity probably due to the deterioration in the HDPE and XLHDPE. However, this deterioration was not easily detectable with tensile and physical appearance.

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