MORPHOLOGY AND TENSILE PROPERTY OF THE BLOW MOLDED HIGH DENSITY POLYETHYLENE (HDPE) AND CROSS-LINKED HDPE BOTTLES AFTER IMMERSION IN PETROL AND DIESEL.

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Polymer are frequently brought into contact with liquids such as chemical products, motor fuels and lubricants because of their varied applications. The effect of petrol and diesel for a period of time on High Density polyethylene (HDPE) and cross-linked HDPE bottles is 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 and 16 weeks before undergoing tests. The temperature for the immersion test used was 23°C and 70°C. Tensile test was carried out to determine the modulus, tensile strength and elongation at break 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. These phenomena correlate with the surface morphology shown by the micrograph. Surface inspection for the morphology property was observed using Scanning Electron Microscopy (SEM). Micrograph analysis showed that the degraded samples undergo brittle failure whereas undegraded samples experienced ductile failure.

INTRODUCTION

Polyethylene is a diverse polymer material used in many products and applications. This diversity is due to the material's ability to be produced with a wide range of properties and characteristics such as impact strength (toughness), chemical resistance, design flexibility, and overall mechanical strength [1]. Plastics are frequently brought into contact with liquids such as chemical products, motor fuel, lubricants, etc depend on their application. 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.

Chemical Stress is really a combination of stress and degradation and happens when the stored chemical oxidizes or plasticizes the polyethylene. In other words, when a chemical leeches electrons from the molecular chain of polyethylene, the chain becomes susceptible to oxygen attack. This in turn will lead, over time, to the embrittlement of the polyethylene [2].

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 [3]. It was found that under certain conditions, some polyethylenes violated the usual time dependent fracture behaviour with respect to the effect of temperature and the quantitative relationship between stress and the failure time [4].

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

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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 [5]

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

METHOD AND MATERIALS

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 HDPE and cross-linked HDPE is used to extrude bottles by using the Extrusion Blow Machine. 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 [6].

Petrol and Diesel Immersion

The samples were immersed in petrol and diesel for 1 day, 1 week and 16 weeks at temperatures 23°C and 70°C. This testing was carried out in accordance to the ISO 175:1999 [7].

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 [6]

Morphology Analysis

The morphology analysis was done at the fracture part of the tensile test samples for the designated temperature and duration. Scanning Electron Microscopy (SEM) was used to look at the fracture part of the tensile test samples. The magnification used is 2000X.

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 last under a predetermined load. A large tensile modulus would indicate that the plastics is rigid and resistance to stretch or elongation [8]. 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 was 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 good impact strength [8].

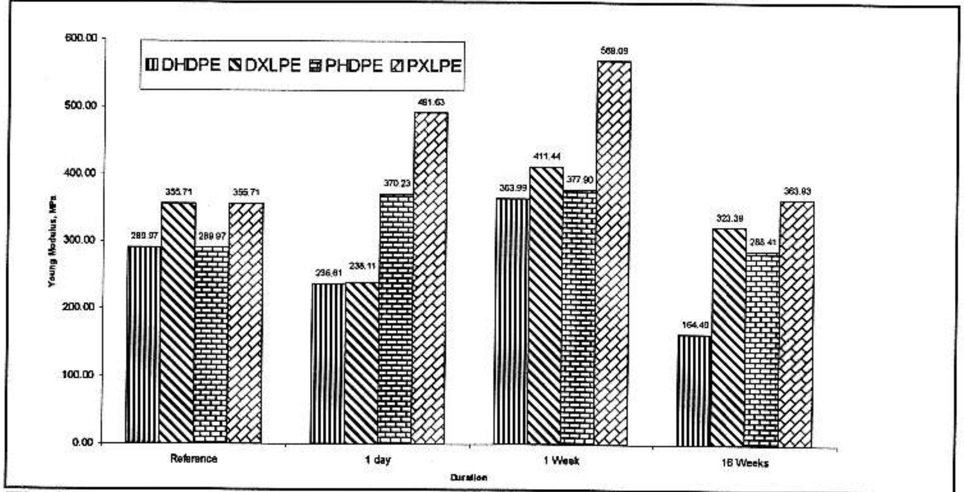

Fig.1. Young modulus for HDPE and XLHDPE immersed in petrol and diesel at 23°C

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.

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%(diesel) after 16 weeks. However 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.

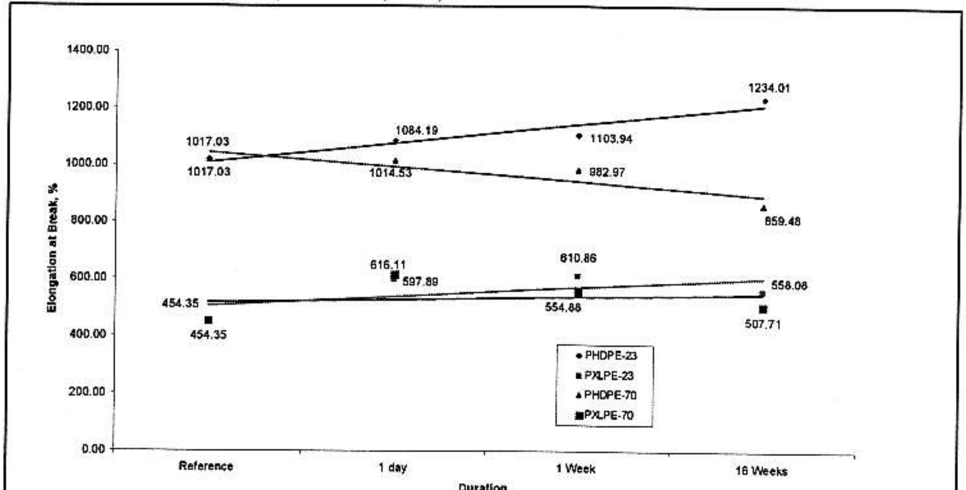

Fig. 2. Elongation at break for petrol immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

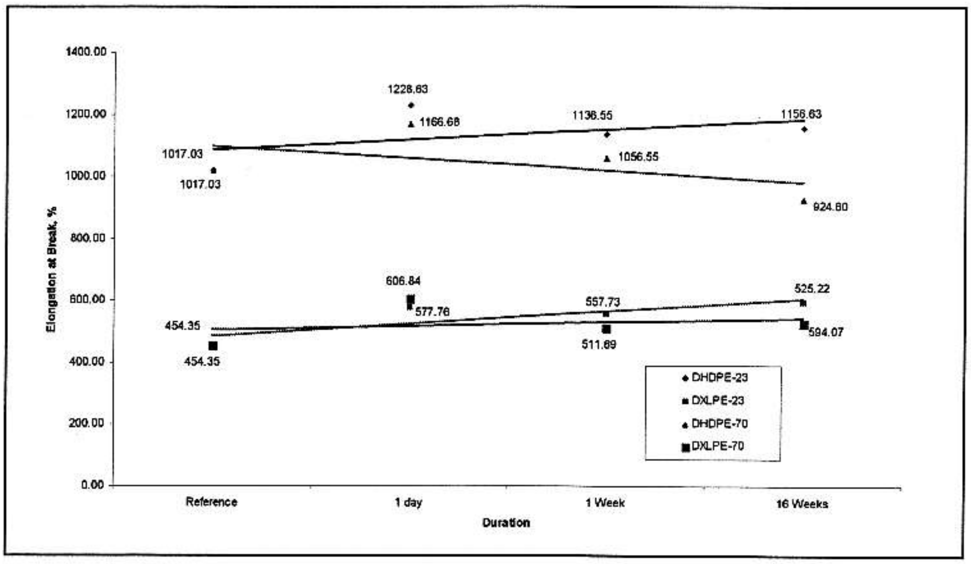

Fig.3. Elongation at break for diesel immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

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 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.

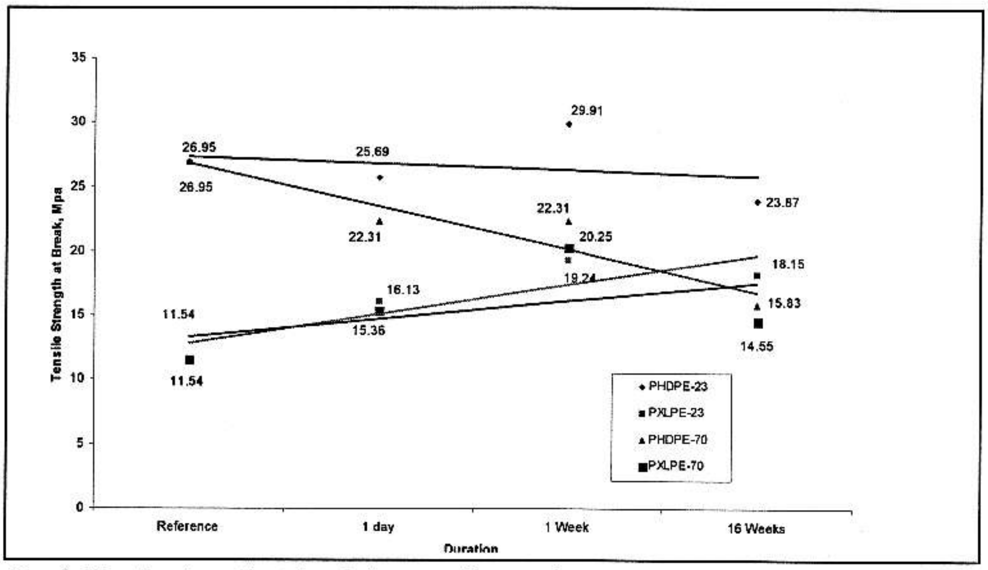

Fig. 4. Tensile strength at break for petrol immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

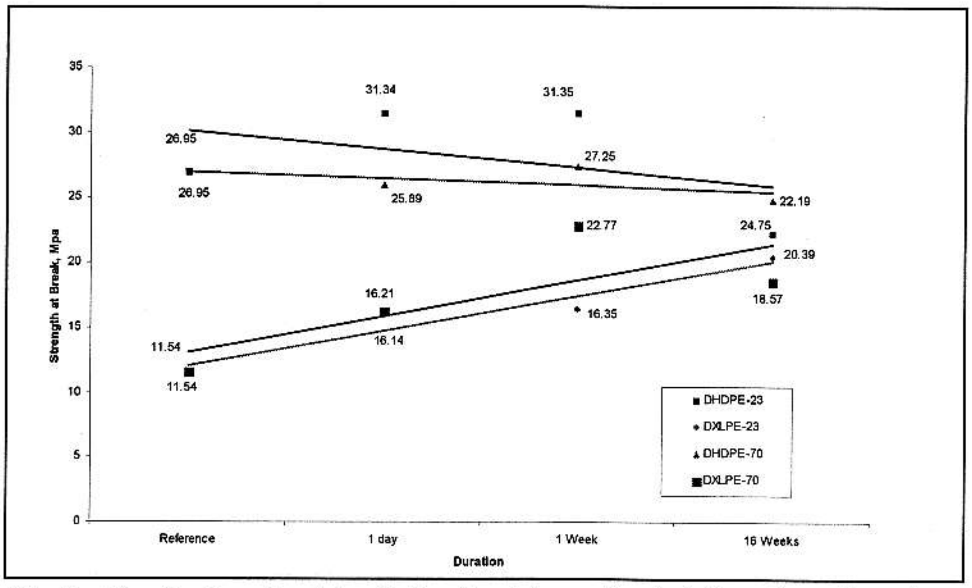

Fig. 5. Tensile strength at break for diesel immersion test from 0 to 16 weeks at temperatures 23°C and 70°C

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 1 week 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, 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, whereas strength of HDPE decreased rapidly after 1 week for both chemicals and temperatures indicating that HDPE start to become unstable or degrade.

The results generally show that the tensile properties decrement in 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.

Morphological Analysis

The SEM micrographs of the HDPE and XLHDPE may relate to the changes in the mechanical properties. Figures 6 and 7 show the micrographs of the HDPE fracture part and XLHDPE which are not immersed in the petrol and diesel. These micrographs showed a rugged and rubbery type of break.

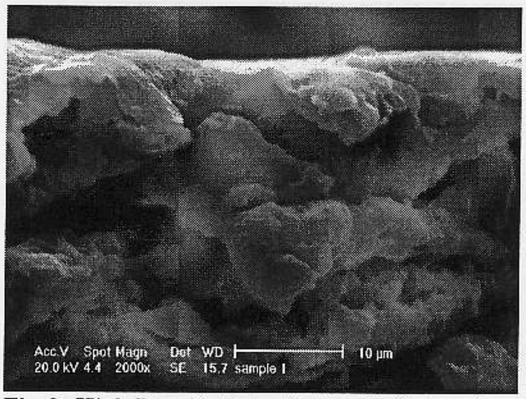

Fig.6. High Density Polyethylene (reference)

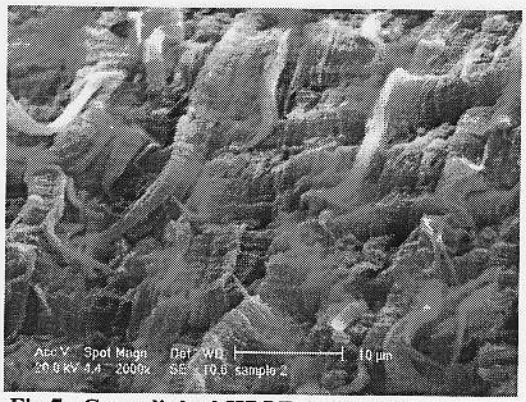

Fig.7. Cross-linked HDPE (reference)

Figures 8 to 19 show the micrographs of the HDPE fracture part and XLHDPE immersed in the petrol and diesel for 1 day, 1week and 16 weeks at 23°C. A ductile failure was observed for the HDPE and XLHDPE for petrol and diesel as shown in the figures. These micrographs showed a rugged and rubbery type of break where by samples elongate and form fibrous structures before final break occurs.

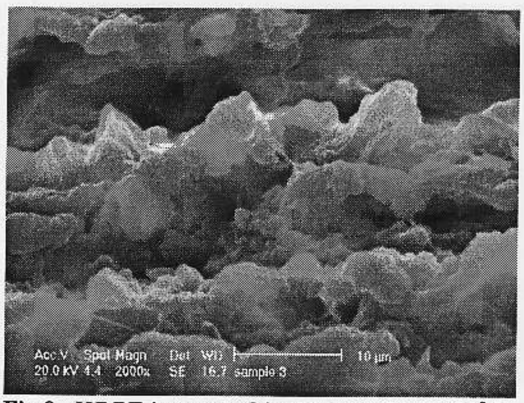

Fig.8. HDPE immersed in Diesel 1 day at 23°C

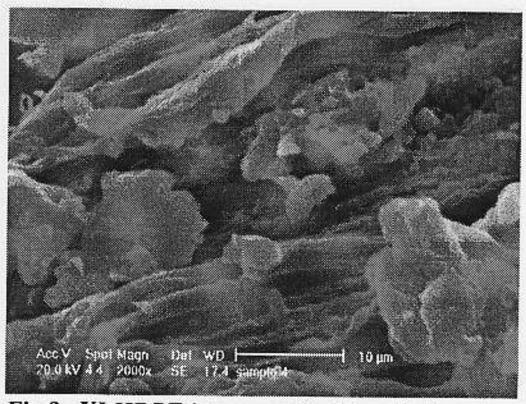

Fig.9. XLHDPE immersed in Diesel 1 day at 23°C

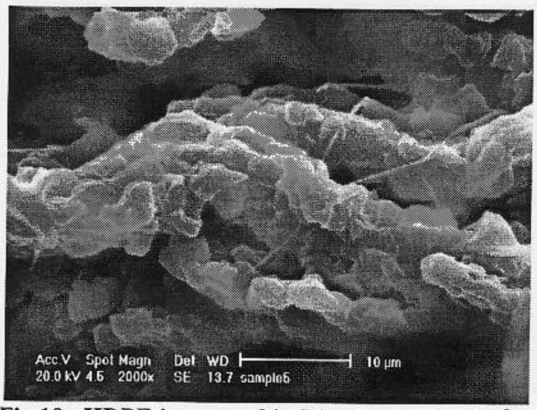

Fig.10. HDPE immersed in Diesel 1 week at 23°C

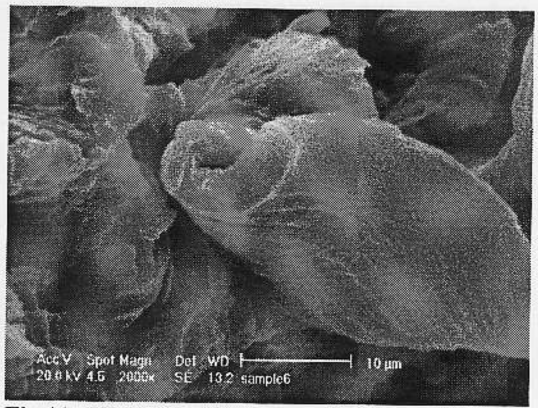

Fig.11. XLHDPE immersed in Diesel 1 week at 23°C

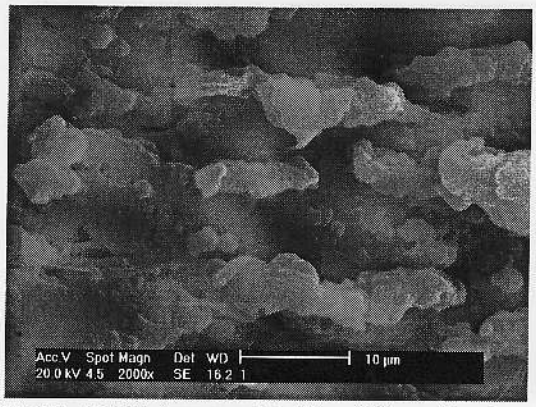

Fig.12. HDPE immersed in Diesel 16 weeks at 23°C

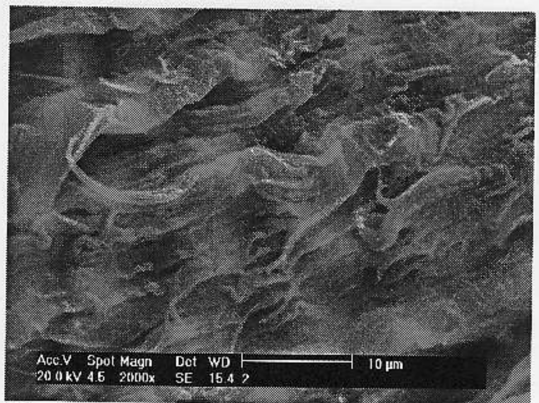

Fig. 13. XLHDPE immersed in Diesel 16 weeks at 23°C

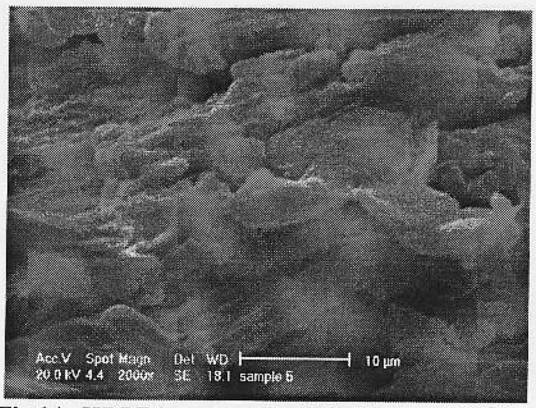

Fig.14. HDPE immersed in Petrol 1 day at 23°C

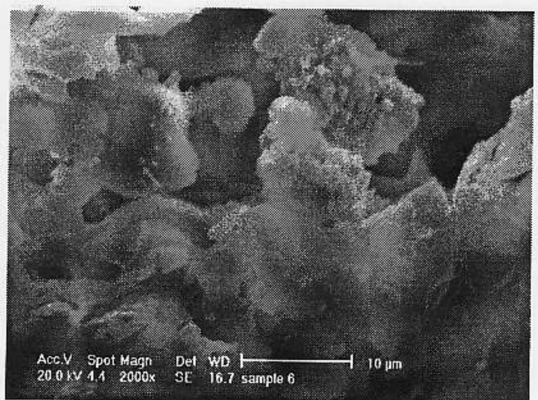

Fig.15. XLHDPE immersed in Petrol 1 day at 23°C

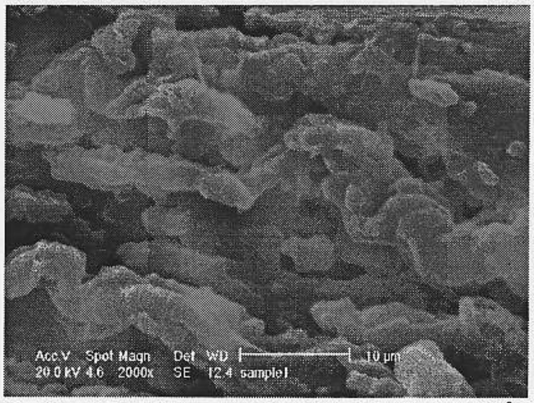

Fig.16. HDPE immersed in Petrol 1 week at 23°C

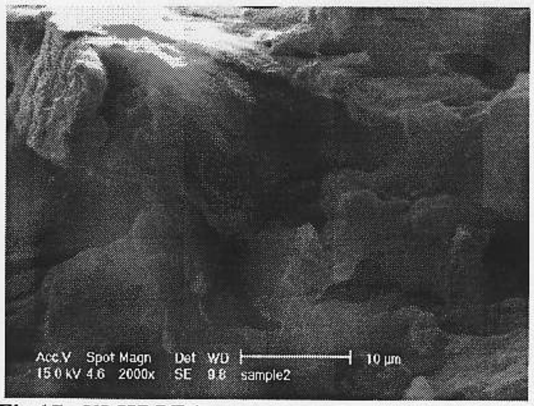

Fig.17. XLHDPE immersed in Petrol 1 week at 23°C

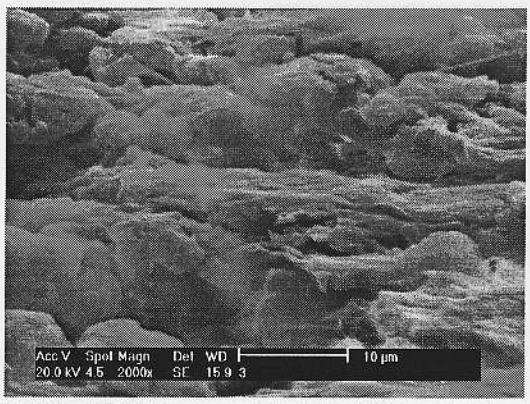

Fig.18. HDPE immersed in Petrol 16 weeks at 23°C

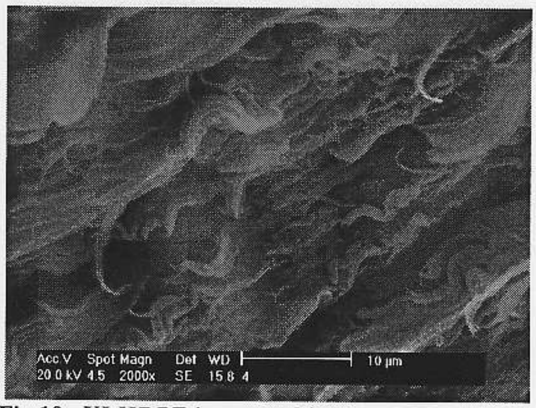

Fig.19. XLHDPE immersed in Petrol 16 weeks at 23°C

Figures 20 to 31 shows the micrographs for fracture part of HDPE and XLHDPE immersed in the petrol and diesel for 1 day, 1week and 16 weeks at 70°C. A ductile failure was observed for the XLHDPE for petrol and diesel. A fibrous and rugged, rubbery fracture surface were seen from the micrograph in figures 21, 23, 25, 27, 29 and 31. For HDPE, ductile failures only occur for samples immersed for 1 day and 1 week for both chemical. However the samples immersed for 16 weeks, brittle failure was observed for both chemical. This indicates that HDPE has low resistance towards petrol and diesel at 70°C, there is easily degraded.

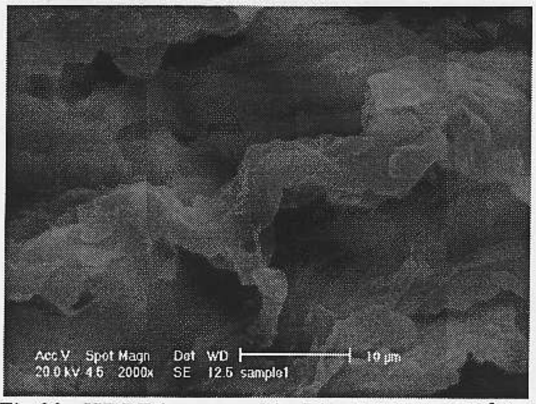

Fig.20. HDPE immersed in Diesel 1 day at 70°C

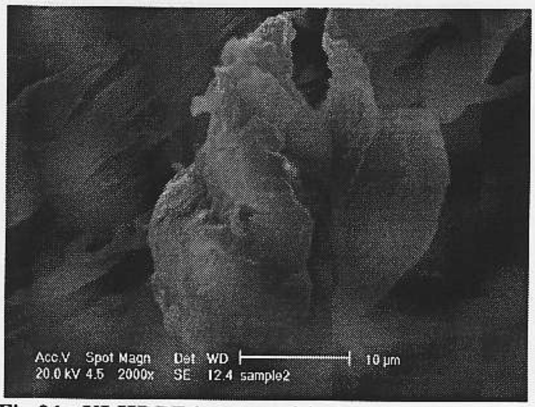

Fig.21. XLHDPE immersed in Diesel 1 day at 70°C

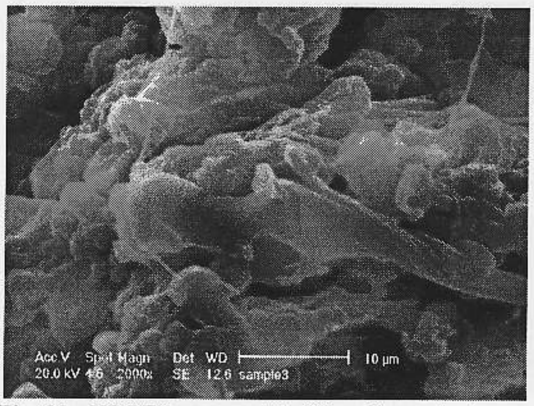

Fig. 22. HDPE immersed in Diesel 1 week at 70°C

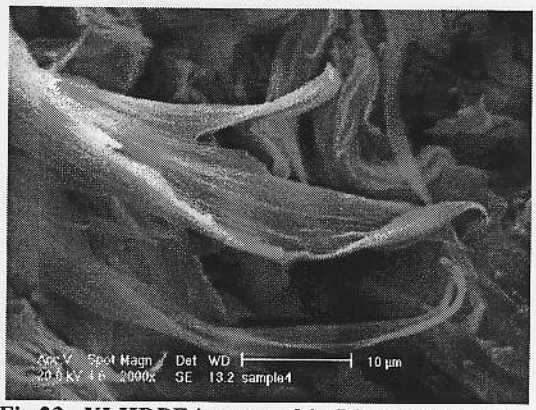

Fig.23. XLHDPE immersed in Diesel 1 week at 70°C

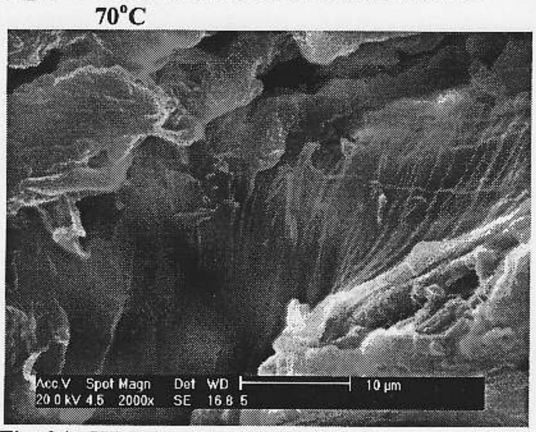

Fig. 24. HDPE immersed in Diesel 16 weeks at 70°C

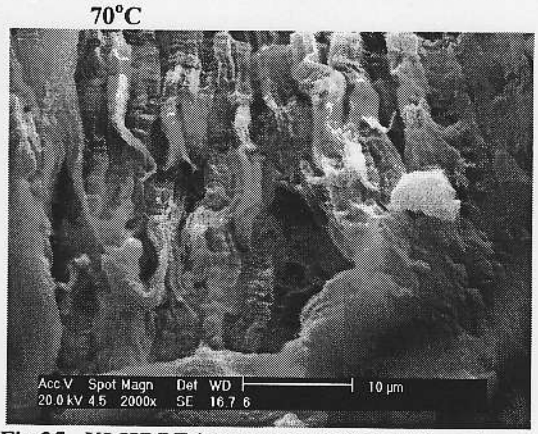

Fig.25. XLHDPE immersed in Diesel 16 weeks at 70°C

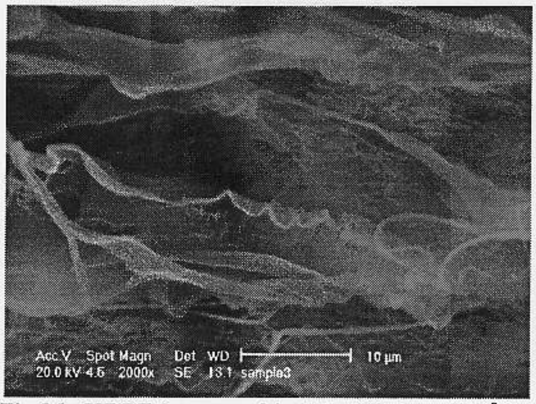

Fig.26. HDPE immersed in Petrol 1 day at 70°C

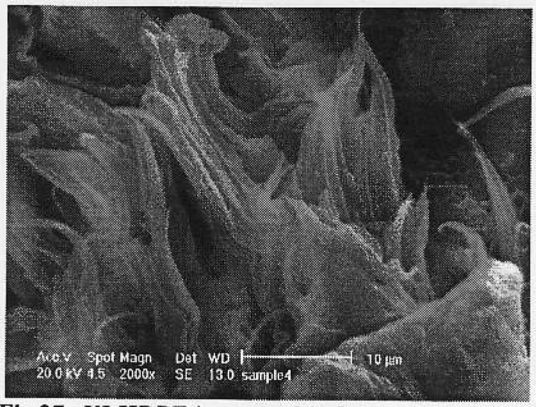

Fig.27. XLHDPE immersed in Petrol 1 day at 70°C

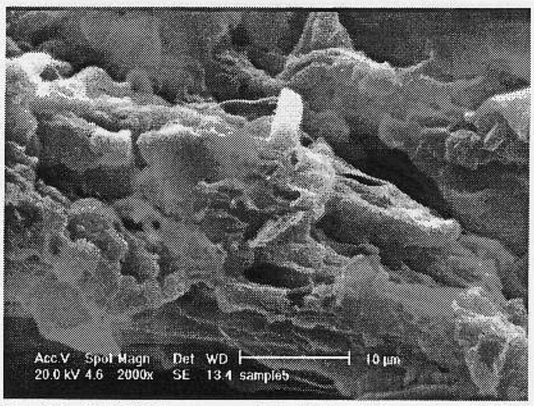

Fig. 28. HDPE immersed in Petrol 1 week at 70°C

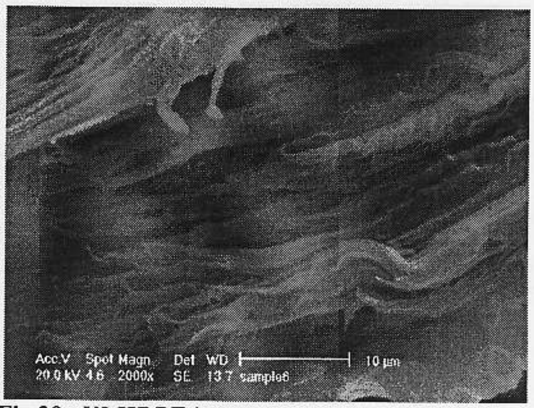

Fig.29. XLHDPE immersed in Petrol 1 week at 70°C

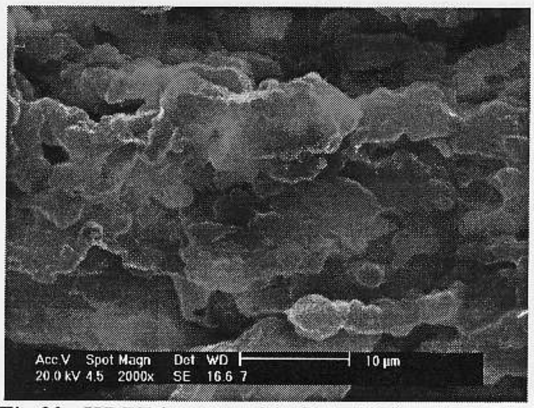

Fig.30. HDPE immersed in Petrol 16 weeks at 70°C

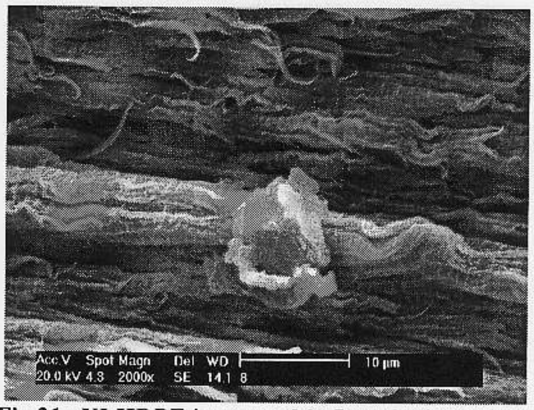

Fig.31. XLHDPE immersed in Petrol 16 weeks at 70°C

Results from the tensile and elongation at break test also support the observed micrographs obtained whereby brittle failure samples gave low stress and strain. Reduction of stress and strain is very dominant in highly degraded samples.

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 have a good resistance to petrol and diesel mostly at ambient temperature, but XLHDPE has greater resistance at 70°C compared to HDPE. Young's modulus of the cross-linked HDPE is higher than HDPE showing that XLHDPE is better in term of stiffness and toughness.

From the SEM micrograph, XLHDPE exhibit a ductile failure, thus HDPE exhibit a brittle failure at high temperature and long duration of immersion for both petrol and diesel. Brittle failures results in smooth and clean break whereas ductile failures show rugged, rubbery and fibrous break.

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