

**CHEMICAL EFFECT ON ROTATIONAL MOLDING GRADE CROSS-LINKED
HIGH DENSITY POLYETHYLENE (XLHDPE) WITH VARYING
CONCENTRATION OF ANTIOXIDANT AND UV STABILIZER**

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ABSTRACT

Chemicals effect from the environment and liquid chemicals (diesel and petrol) on rotational molding grade (HD3840UA) high density polyethylene (HDPE) and cross-linked HDPE samples were studied according to ASTM D1435 and ISO 175: 1999. The HDPE (pure) and cross-linked HDPE samples with various antioxidant concentrations (0.0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%) were prepared. Samples were immersed in the liquid chemicals at 23°C for the immersion test. The weathering test was conducted to study the effected of chemical in the environment by exposing the samples to the natural atmosphere. The duration of the test is 1 day, 1 week and 8 weeks. Tensile test was carried out according to ASTM D638-02 to determine the stress at break, elongation at break and Young's Modulus. The changes in weight and dimension were also determined. The tensile properties result show that the rate of degradation for the petrol immersion is more than diesel immersion at 23°C for both HDPE and cross-linked HDPE samples. Both samples experienced apparent reduction in the tensile properties within 24 hours, regardless of antioxidant concentrations. Physically the sample immersed in diesel shows a higher swelling ratio. The HDPE is more susceptible to liquid chemical as well as atmospheric attack. The cross-linked HDPE with optimum level of antioxidant contents is the most stable towards liquid chemical and environmental attack.

Keywords: HDPE, Cross-linked HDPE, Antioxidant, UV Stabilizer, Chemical Effect

INTRODUCTION

A common polymer is vulnerable to many defects of nature, including UV degradation, temperature defects, chemical attack as well as swelling and stressed phenomenon. Exposing polymer to the environment may results in the deterioration caused by the combination of all

weather factor, including solar radiation, heat/cold, moisture (solid, liquid and vapor), oxygen and atmospheric contaminants not only on the polymeric itself but also other components within the matrix such as additives, dyes and stabilizers [1,2].

Common air pollutants include sulfur oxides, hydrocarbons, nitrogen oxides and particulate matter such as sand, dust, dirt and soot. Some of these may react with organic materials but have a much more severe effect in combination with other factors. Example rapid discoloration of pigments as well as crosslinking and embitterment of material. The deterioration, chemically and environmentally, depends on the specific wavelength and amount of solar radiation the polymer are capable of absorbing. The strength of their chemical bonds in relation to the photon energies of the solar radiation absorbed and the reaction processes promoted by heat, moisture (including chemical contaminants) and other factors following bond breakage. Complex interactions of the combination of the environment factors with the polymer and its components result in irreversible exposure changes in the chemical structures and physical properties that generally changes both the appearance and mechanical properties and reduces the useful life of the material [3]. High density polyethylene (HDPE) upon weathering and liquid chemical imposes property defects or deterioration.

By the introduction of some methods, such as silane technology in the polyethylene resins, the cross-linked structure can be achieved in order to increase its original properties. This cross-link exists as a primary bond, which are chemically attached to the polyethylene chains. These cross-linking facilities will further improve the long-term performance as it [4].

Antioxidants are employed to inhibit or reduce the rate of oxidative degradation of polymers. Therefore, they extend the service life of the polymers at ambient temperature and increase the stability of the polymers at higher temperature [5]. Oxidative degradation is most prevalent on the surface and significantly reduced toward the center due to the limited supply of oxygen in that region. The penetration of oxygen into the polymer is related to its rate of diffusion which depends on temperature, polymer chemical structure and morphology. Oxygen enhances the effect of solar radiation. UV stabilizers are added to polymers to protect them from UV radiation which is one of the critical factors that initiates reaction and bond breakage resulting in a process known as photodegradation. The first way that many UV stabilizers work is to absorb the UV energy and then dissipate it in a harmless form. Another way that the same stabilizers might protect a polymer from UV radiation is by 'quenching' a macromolecule that has been excited to a higher energy level. The UV stabilizer may draw energy away and dissipate it as a heat. A third mechanism is through accepting free radicals from UV exposure [6,7].

EXPERIMENTAL

Materials

HDPE of grade Etilinas HD 3840UA and the supplied by Polyethylene (M) Sdn Bhd was used to prepare the crosslink HDPE. Ethylene Vinyl Acetate (EVA) from The Polyolefin Company Singapore was used in the master batch preparation which later used to prepare the HDPE antioxidant formulations. EVA was used as a carrier for the master bath because of the lower processing temperature needed in compounding process, so the antioxidant and UV stabilizer will not lost at the state preparing master bath. Furthermore EVA is compatibility with the polyolefin. The antioxidants are Irganox 1035, Irganox PS 802 and UV stabilizer Chimassorb 119 FL, from Ciba Speciality Chemicals. The petrol and diesel used were from Petronas petrol station.

Sample Preparations

Master batch

Master batch is first prepared with the formulation as shown in Table 1. It is compounded in a twin screw extruder with screw temperature between 130°C -150°C. The extrudate formed was cut into pellets by using a pelletizer and later used to formulate samples with various antioxidant content as shown in Table 2. The combination of the master batch which consist of Irganox 1035: Irganox PS802: Chimassorb 119FL is in the ration of for 1:1:1.

Table 1: Masterbatch formulation

Material	Concentration (phr)		
Ethyl Vinyl Acetate (EVA)	100	100	100
Irganox 1035	5	0	0
Irganox PS 802	0	5	0
Chimassorb 119FL	0	0	5

Table 2: HDPE samples formulation

Sample	Concentration (phr)		
	HDPE (HD 3840UA)	Silane Cross-linking Agent	Master Batch
HDPE	100	0	0
XLPE (0.0% AO)	100	2.0	0
XLPE (0.1% AO)	100	2.0	2.1
XLPE (0.2% AO)	100	2.0	4.2
XLPE (0.3% AO)	100	2.0	6.3
XLPE (0.4% AO)	100	2.0	8.4
XLPE (0.5% AO)	100	2.0	10.5

The samples formulation from Table 2 was extruded into the tape for tensile test.

Curing

Curing is a process to crosslink the samples. This process is accomplished by immersing the samples in hot water for a day at 100°C to gain the maximum cross-linked samples [8].

TESTING AND ANALYSIS

Petrol and Diesel Immersion

The immersion tests were carried out according to ISO 175:1999 (Standard Methods of Test for the Determination of The Effect of liquid Chemicals) [9] for the HDPE and crosslinked HDPE. These immersion tests were conducted at 23°C ± 2°C in a 5L beaker with the aluminium foil enclosure. The durations used for the immersion test are 24 hours, 1 week and 8 weeks. The samples were tested fortnightly until the eight for its physical and tensile properties.

Tropical Weather Testing Method

This test was carried out according to ASTM D 1435 (Standard Method for Natural Weather Test) [10]. The main purpose of this test is to identify the effect of tropical weather on HDPE and cross-linked HDPE samples. Thus, samples were hung on the rack which was located in open air environment. These samples were tied at the edge and were exposed to outside weather for 24 hours, 1 week and then for 8 weeks. Once the exposure time is over, these samples were cut into dumbbell shape for the tensile test.

Tensile Test Method

The tensile test was carried out according to ASTM D 638-02 [11] by using LLoyd tensile tester, Model EZ 20 at a cross-head speed of 10mm min^{-1} . Dumbbell shaped specimens with cross-sectional area of approximately $3.2 \times 0.8\text{ mm}$ and gauge length of 7.62 mm , were used for the measurements. Five dumbbells per blend sample were used for each analysis and the average was taken as the reported value.

RESULTS AND DISCUSSION

Physical Properties

Changes in Weight

Figures 1 and 2 illustrate the effects of antioxidant on diesel and petrol immersion for changes in weight test. Basically as the concentration of antioxidant increases in the crosslinked HDPE, the percentage change in weight does not vary much, there is within an experimental error of $\pm 1\%$ at all time duration. After 24 hours of immersion, the % of weight changes for HDPE was 3.57% in diesel, whereas for the counterparts immersed in petrol, the changes are only 1.97%. Similarly, throughout the duration, higher changes were obtained for HDPE samples immersed in diesel compared to petrol. For the sample with 0.1% of antioxidant concentration, the percentage change in petrol is 1.03% whereas for immersion in diesel it is 2.42%. This indicates that diesel has a stronger attack toward HDPE compared to petrol. However, between HDPE and cross-linked samples, the HDPE has a higher weight change than cross-linked HDPE in both diesel and also petrol throughout this immersion

period. Therefore, from the results antioxidant concentration is not affecting the performance of the cross-linked HDPE at all immersion time, but, it is affected by the level of cross-linking. The cross-linked HDPE samples have chemical bonds which act as chemical resistance and this prevent the solvation from occurring. The HDPE samples which contain only physical bonding between the chains are considerably weak, thus, chain breakages easily occur and this lead to the swelling of sample. Eventually, the free volume between the chain structures will increase and this will lead to a higher absorption rate of liquid chemical and causes swelling rate to increase.

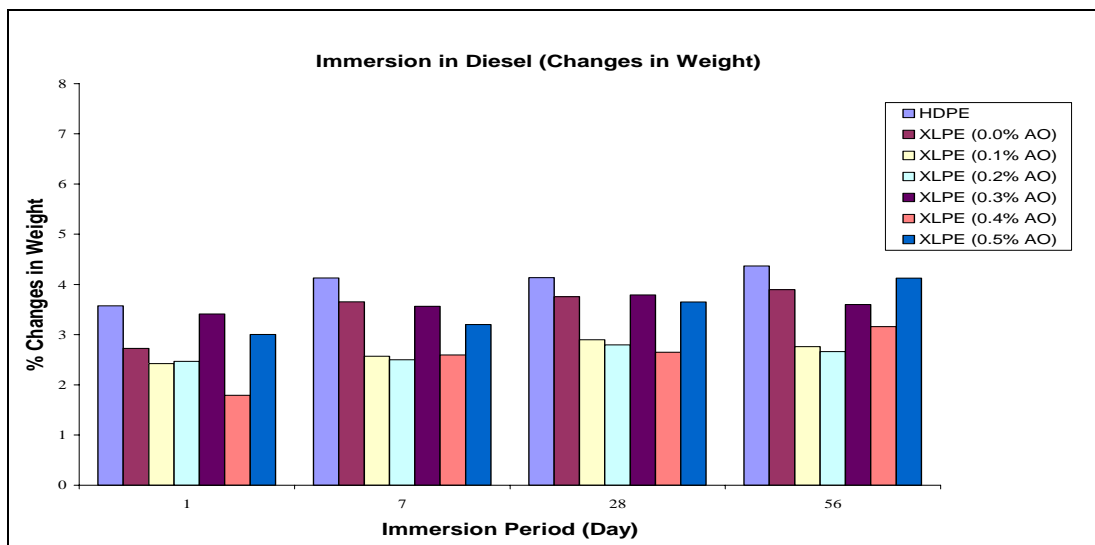


Figure 1: Changes in Weight for the samples immersed in Diesel at 23°C

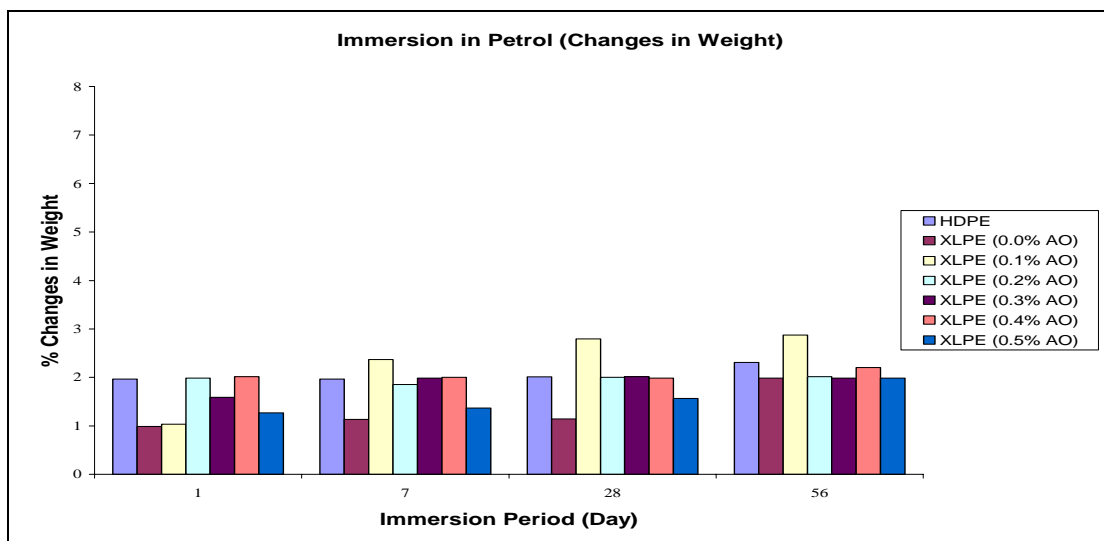


Figure 2: Changes in Weight for the samples immersed in Petrol at 23°C

Changes in Length

Another important physical test on HDPE and cross-linked HDPE samples are length changes.

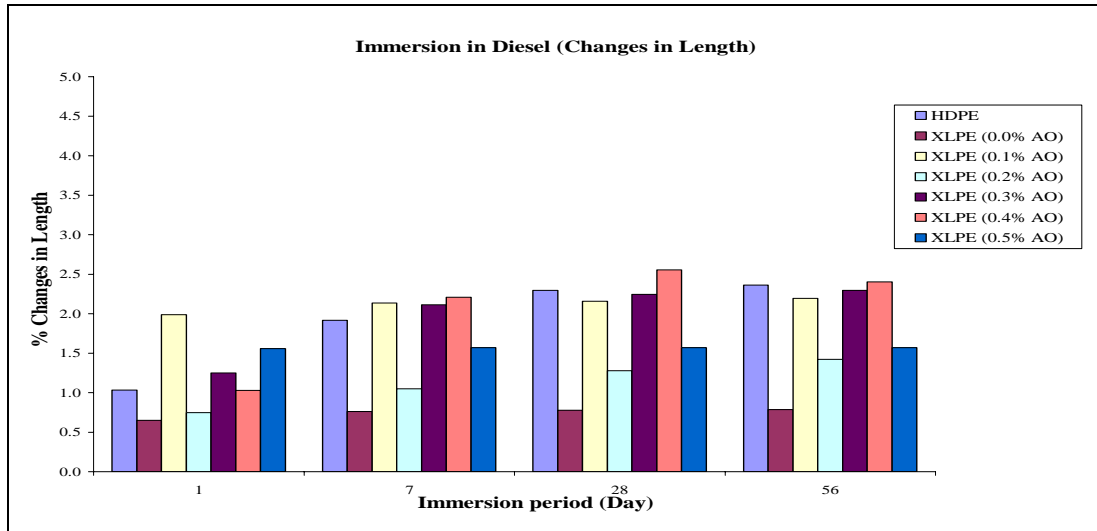


Figure 3: Changes in Length for the samples immersed in Diesel at 23°C

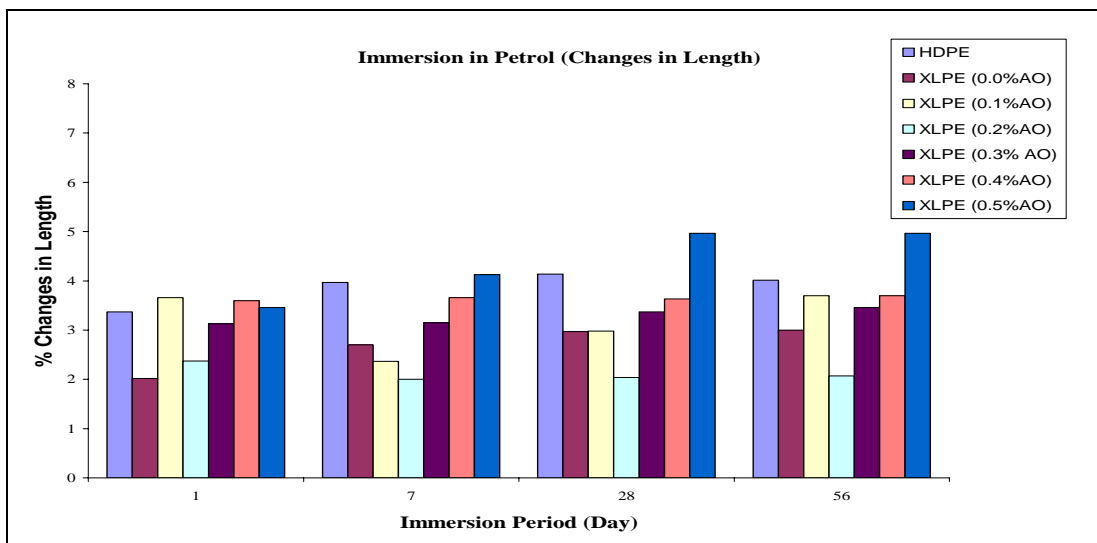


Figure 4: Changes in Length for the samples immersed in Petrol at 23°C

Figures 3 and 4 show the changes in length for both immersion in diesel and petrol increased slightly throughout the period. However, the HDPE samples displayed higher changes in length compared to cross-linked HDPE. This is because cross-linked sample has a higher resistance towards chemical attack whereas the HDPE sample has poor resistance towards the liquid chemicals.

Tensile Properties

Immersion in Diesel

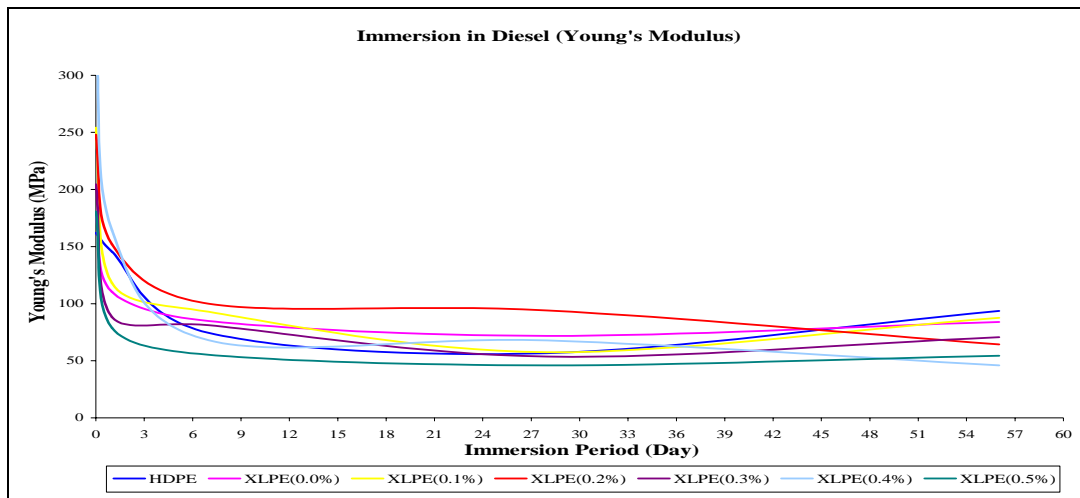


Figure 5: Young's Modulus for the samples immersed in Diesel at 23°C

Figure 5 shows the variation of Young Modulus for both HDPE and cross-linked HDPE with different concentration of antioxidants in the immersed environment at 23°C with diesel. Generally, the change properties were detected at the early stage of immersion period. However, these changes were not significant after 1 week of exposure.

The HDPE and cross-linked HDPE samples experience a drop in modulus at the early immersion stage and remain unchanged up to 39 days. However, the cross-linked HDPE shows a higher value of Young's Modulus than HDPE at the end of the immersion period. This is probably because the cross-linked HDPE has higher resistant to chemical attacks due to its chemically bonded linkages which prevent solvation from occurring. Meanwhile, modulus drop is seen in HDPE throughout the immersion period. The HDPE only contains physical bond between chains which hardly withstands the liquid chemicals. The presence of antioxidants slightly decreases the modulus compared to cross-linked HDPE without antioxidant due to the existence of EVA in the mixture of antioxidants which give the elasticity effect. The amount of EVA added was proportional to the concentration of antioxidant. Thus, the sample with higher antioxidant concentration exhibits better elastic properties.

For sample cross-linked HDPE immersed in diesel, the stress at break decreases drastically at the early period of immersion which then remain constant throughout the immersion period as supported by the swelling phenomena and Figure 6. It can be deduced

that the plasticity of the specimen has increased [12], this specimen is affected by the plasticizing characteristics of diesel. The constant stress at break suggests no bond breakage has occurred, though swelling has been detected. The reduction in stress at break (Figure 6) for HDPE outweighs that of XLPE (10.5 % compared to 7.9 %). The absorption effects of diesel are more significant in HDPE compared to cross-linked counterparts. This suggests that cross-linking plays an important role in maintaining the strength of the polymer. The lack of such supporting bonds has caused HDPE to be weaker in terms of tensile properties. The chemical attack and severe bond breakage are not the cause for the property reduction but due to the plasticizing effect of diesel. Consequently, cross-linking of HDPE helps to strengthen the polymer against diesel attack. The change in strain at break (Figure 7) shows similar behavior as stress at break.

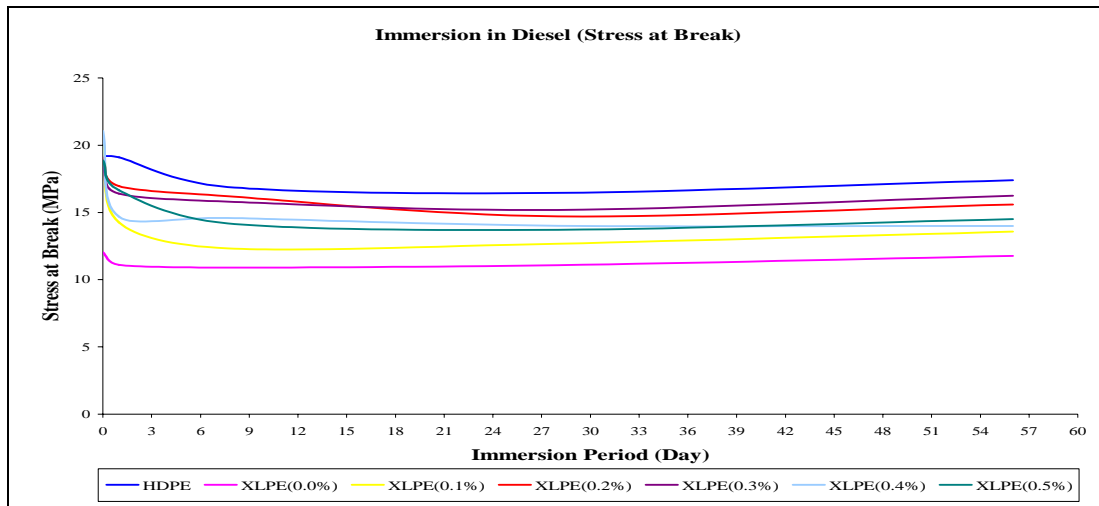


Figure 6: Stress at Break for the samples immersed in Diesel at 23°C

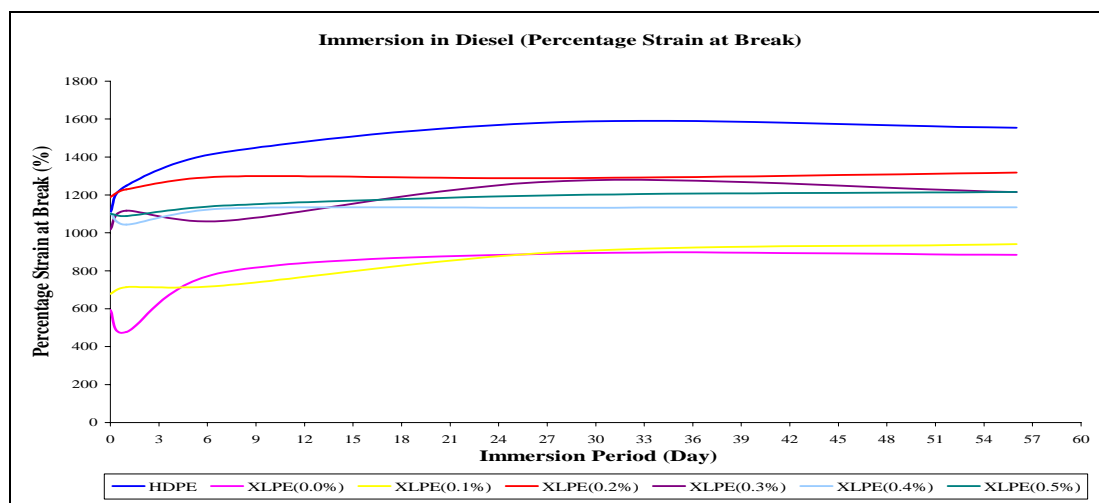


Figure 7: Percentage Strain at Break for the samples immersed in Diesel at 23°C

The decrease of modulus and increase in the elongation is related to the plasticizing effect of the HDPE samples. The polymers have become softer and less rigid. This phenomenon is indicated upon 2 factors. Firstly, the presence of EVA additive in the antioxidants tends to plasticize the polymer molecules by reducing intermolecular friction and promoting mobility. The presence of diesel molecules within polymer structures plays the role of a plasticizer. The bond breaking due to diesel within the polymer chains are not detected. Therefore, it is deduced that the variation in stress and strain at different antioxidant concentration are mainly due to the changing content of EVA in the antioxidants and the diesel molecules produce similar effect but their role in this phenomenon is limited.

Immersion in Petrol

Figure 8 shows the changes in the Young's Modulus for cross-linked and uncross-linked HDPE in the immersion of petrol at 23°C. Basically similar results were observed as for the immersion in the diesel. The changes of tensile properties with time of exposure finally reach a constant asymptote.

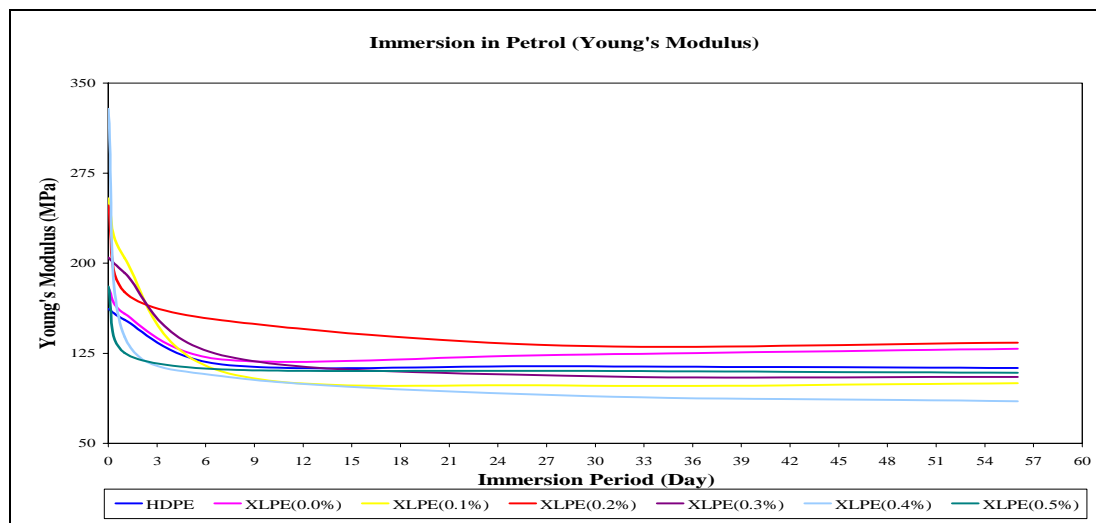


Figure 8: Young's Modulus for the samples immersed in Petrol at 23°C

HDPE is most affected by petrol immersion phenomenon. A sharp decrease in Young's Modulus was observed (29.6%). The stress at break (Figure 9) for this specimen experienced the highest loss of 33.9%. There was also a significant increase in elongation at break (12.5%). For XLPE the modulus change is almost similar to HDPE (31.04%). However, the elongation at break (Figure 10) and stress at break were much deviated (34.38% and 6.67%). Since, the presence of chemical linkages have contributed to the strengthening

effects seen in the crosslinked HDPE sample. Thus, petrol has similar effect of plasticizing the polymer molecules. The effect of bond-breaking and degradation by chemical attack were not present. This was concluded from the long term exposure at the temperature of 23°C analysis, no changes in properties were detected for any sample.

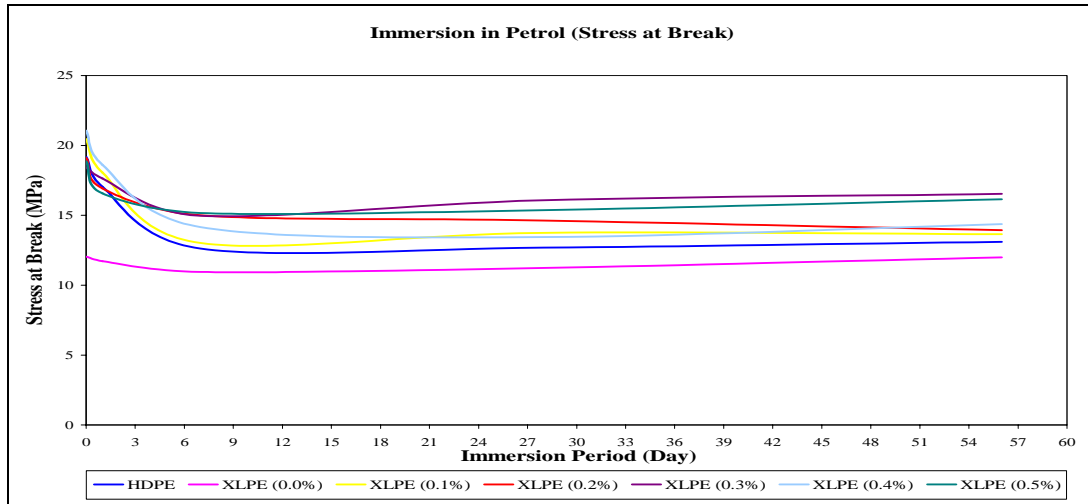


Figure 9: Stress at Break for the samples immersed in Petrol at 23°C

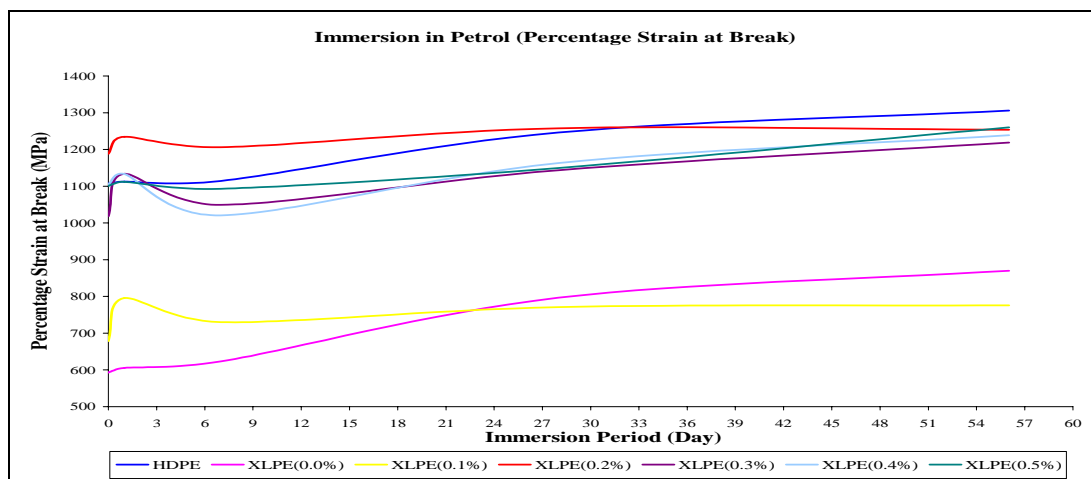


Figure 10: Percentage Strain at Break for the samples immersed in Petrol at 23°C

Tropical Weathering

Some of the important parameters which were mainly affecting the properties are sunrays, high temperature, atmospheric pollutants, rain as well as high humidity.

Figure 11 shows the HDPE and cross-linked HDPE samples which were exposed to the atmospheric weather for the period of 8 weeks.

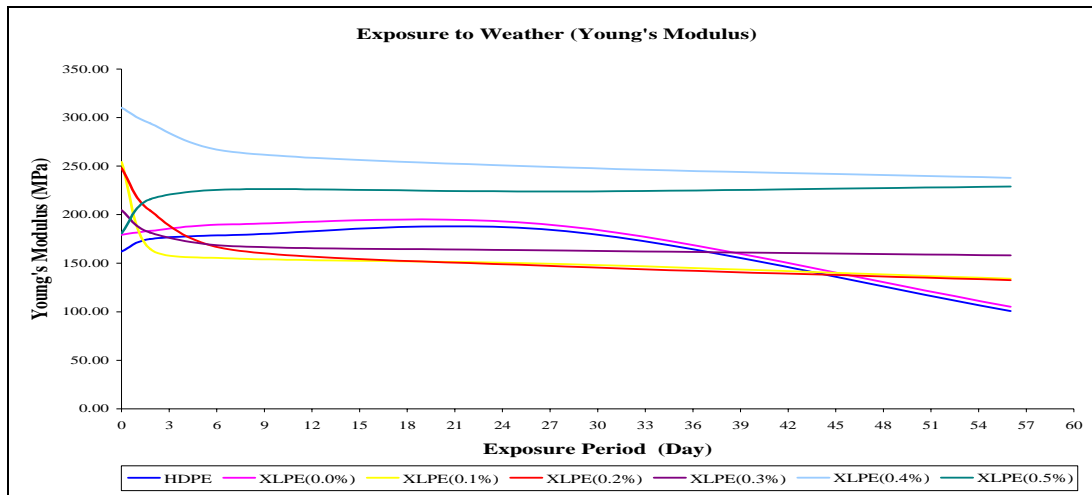


Figure 11: Young's Modulus for the samples exposed to the natural weather

It can be observed that HDPE and cross-linked HDPE without UV stabilizer are badly affected by weathering. Young's Modulus Figure 11, for the sample with 0.5% of UV stabilizer concentration shows a slight increment throughout the period (8.03%). Meanwhile, the samples without UV stabilizer were drastically decreased after 4 weeks of the exposure. The percentage reduction is estimated to be approximately 44.01%. This clearly shows that the samples without UV stabilizer are prone to the degradation process. The stress at break Figure 12, for both samples decreases with exposure time.

For strain at break, Figure 13, HDPE shows a slight increase in elongation whilst cross-linked HDPE without UV stabilizer suffers reduced elongation. For HDPE, softening has occurred during weathering, this could be related to the increase in the amorphous region due to rapid heating and cooling of atmospheric temperature. The reduction in modulus is related to the internal chain rupture due to UV degradation effects. For the cross-linked HDPE, embrittlement is obvious. Internal crosslink and backbone rupture is predictable. The presence of UV stabilizer shows resistive characteristics against weathering effects. The tensile behaviors of the sample with 0.5% of UV stabilizer concentration are considerably constant throughout the exposure time. So it can be concluded that, this cross-linked HDPE sample is excellent in withstanding the weathering effects. However, the samples with a lower concentration of UV stabilizer (0.2%, 0.3% and 0.4%) are also estimated as a good weather resistance compared to the one without UV stabilizer.

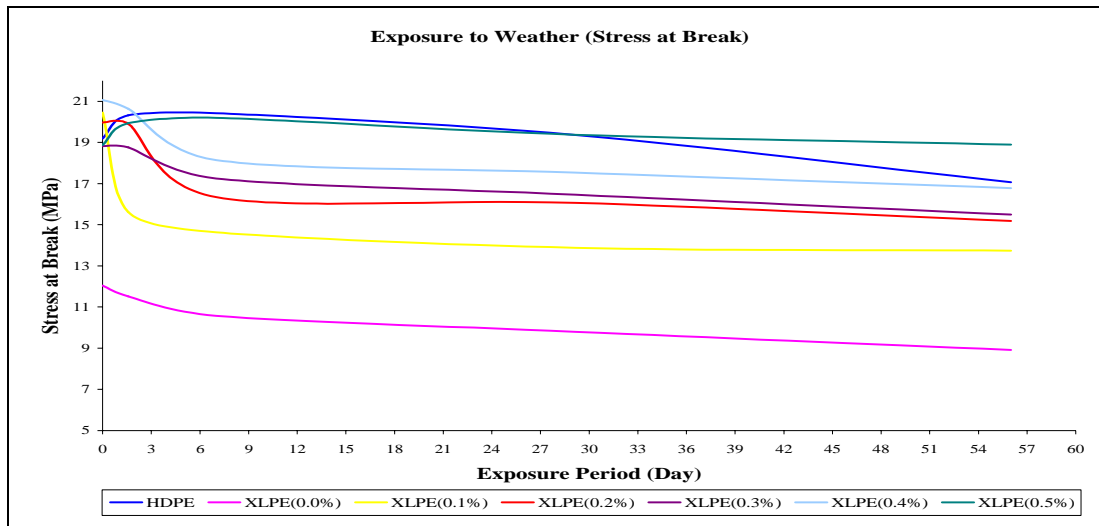


Figure 12: Stress at Break for the samples exposed to the natural weather

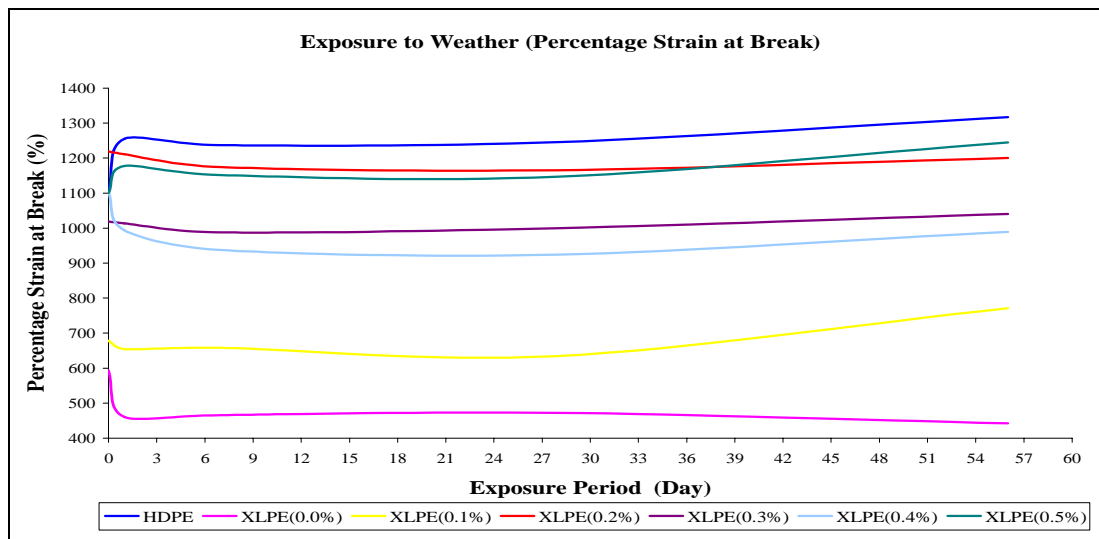


Figure 13: Percentage Strain at Break for the samples exposed to the natural weather

CONCLUSION

The HDPE and cross-linked HDPE samples, which have been immersed in petrol and diesel, experienced a swelling phenomenon with respect to time, and apparent changes were discovered only for samples immersed in diesel. Cross-linked HDPE has a better resistance towards liquid chemicals compared to HDPE. The antioxidant concentration does not have much effect upon liquid chemicals. However, the changes are basically related to the presence of EVA in the antioxidant mixture that acts as plasticizer to change the tensile behavior.

Petrol and diesel, act as a plasticizer increasing the strain properties and decreasing the stress at break as well as Young's Modulus. Generally cross-linked HDPE has higher mechanical properties compared to HDPE.

Weather factors considerably change the tensile properties. Samples with higher UV stabilizer concentration exhibit a better resistance towards outside weather. Weathering caused embrittlement and surface stress and cracks.

. Hence, cross-linked HDPE with optimum level of antioxidant are stable to wards liquid chemicals, retaliates better against bond-breaking forces and environmental attack.

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