On the Environmental Stress Cracking Resistance of High Density Polyethylene (HDPE)

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Abstract: This research reports a visualization investigation of environmental stress cracking (ESC) of a high-density polyethylene (HDPE) prepared in house and a commercial high-density polyethylene. The in house made HDPE showed an excellent resistance against ESC as none of the tested samples cracked under chemical solution and that was due to higher value of molecular weight and less percentage of chain branching. On the other hand, the commercial HDPE had poor resistance against ESC under chemical solution, as all tested samples was cracked and completely splitted up into two pieces. An interesting finding of this research was that the commercial HDPE of relatively lower molecular weight cracked when stressed within the environment of ordinary water. Finally, this research recommended a thorough investigation of the role of additives and fillers on the ESC resistant of Polyethylene.

Keywords: Polyethylene, Environmental stress cracking, Molecular weight, Additives.

INTRODUCTION

Catastrophic failure of plastics may occur due to initiation and propagation of micro cracks when plastics are stressed in the presence of various liquids varying form soft to aggressive such as water, detergents and alcohols. The susceptibility of a plastic article to failure due to slow crack growth when surface contacting with liquids is known as environmental stress cracking (ESC). Polyethylene (PE) is known for its low resistance to cracks initiated by solutions and liquids when put in service such as in landfill lining or geo-membranes and cable insulation.

Factors affecting ESC include molecular weight (MW) and its distribution (MWD), chain branching, degree of crystallinity, density, catalyst type and monomers used.

ESC may lead to hole creation in the HDPE geo-membrane liner which would cause gas and leachate escape out of the landfill [1]. Earliest theoretical analyses of ESC in PE have been reported by various authors in the past, *e.g*. Marshall and coworkers [2] and Brown [3]. Marshall *et al*. [2] introduced a relationship between stress intensity factor, Ki and crack or flaw speed, à using fracture mechanics technique to study ESC for PE. Brown [3] suggested that ESC of PE is due to stress induced swelling of the amorphous part of PE. ESC resistance for a low molecular weight HDPE was found to increase with annealing between 85°C and 115°C [4]. A kinetic for ESC in HDPE may be found elsewhere [5].

It is known that as melt flow index (MFI) of a polymer decreases, MW increases and leads to improvement in ESC resistance (ESCR), however one should be cautious about the shape of the MW distribution. When poly-disparity index (PDI) of HDPE increases, ESCR increases as well [6]. Note here that MFI may not be related to number average molecular weight (M_n) but rather to PDI or weight average molecular weight (Mw) [6-7]. In general, it has been postulated by others [6] that ultra-high molecular weight species content in HDPE may lead to a suppression in void growth in the presence of a surface-active agent and hence ESCR may be increased [6]. From a molecular structure point of view, some important morphological aspects can greatly affect ESCR of PE such as inter-lamellar linkages in form of tie molecules [8] and physical chain entanglements [7]. Some sparse studies appeared in the literature tried to improve ESCR of HDPE by blending and compounding with other polymeric materials and fillers such as PE and wood [9-11]. It was reported that blending HDPE with up to 50 wt% of LDPE and LLDPE may significantly increase time to failure for the ESC specimens [9]. ESCR of HDPE was more pronounced when it was blended with LLDPE due to co-crystallinity effect that influences amorphous phase mobility of HDPE [9]. Khodabandelou *et al*. [10] have reported that ESCR of high impact polystyrene (HIPS) can be significantly increased by blending with 10 wt% of HDPE in the presence of a proper compatibilizer. Compounding of HDPE with wood flakes was not found to alter ESCR of HDPE [11].

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EXPERIMENTAL

Materials Used

HDPE (HDPE-276) used in this study was custom synthesized according to a previous study [12]. It is a zirconium based single site catalyst with a high molecular weight value. A commercial blow-molding grade HDPE was also used to compare its ESCR with that of the custom synthesized HDPE-276. The commercial HDPE (HDPE-C) was a courtesy of Saudi basic industries corporation (SABIC) in Riyadh, Saudi Arabia. Table **1** gives some properties of used HDPEs.

Melt Flow Index (MFI)

Melt flow index or fluidity of the polymers used in this study was measured by a melt flow indexer (MFI 10 by Lloyd Davenport, UK). Four consecutive readings of the MFI were taken and the average of these readings was recorded.

ESCR Measurements

ESCR tests were performed in accordance with ASTM D1693 (Environmental stress cracking (ESC) for polyethylene plastics). Test samples were prepared by compression molding of HDPE pellets in molten state (~260 °C) using a carver hot press. The dimensions of a sample bar are illustrated in Figure **1**. A controlled notch is cut horizontally across each sample, which serves as a crack initiation point. The samples were bent and inserted into a “C” shaped bracket as a sample holder, creating a stress in the specimen (Figure **2**). The sample holder that contains ten bent plastic samples is inserted into a tube filled with IGEPAL® solutionI GEPAL® solution 10 % (Nonylphenoxy polyethyleneoxy/ethanol). The tube is then placed into a water bath capable of providing controlled heated environment for the samples (50 °C). After that, samples are inspected periodically for visible cracking or complete failure.

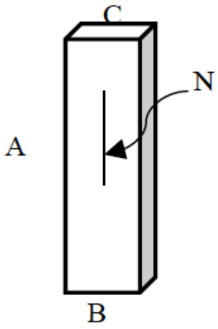

Figure 1: Test sample dimensions: length (**A**) = 38 mm, depth (**B**) = 13 mm, width (**C**) = 1.85-1.95 mm, notch depth (N) = 0.3-0.4mm.

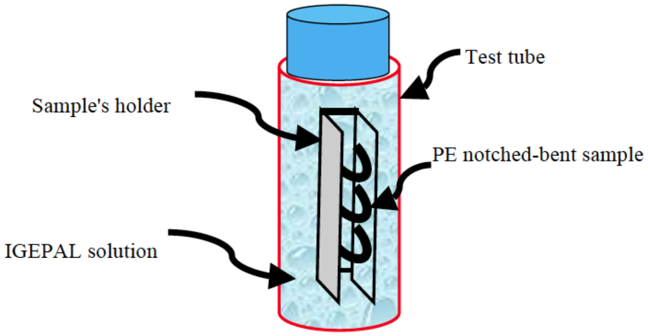

Figure 2: Test samples bent and immersed in the solution.

RESULTS AND DISCUSSIONS

Table **2** gives the results of ASTM D1693 experiments performed for both HDPE-C and HDPE-276. It is seen from Table **2** that HDPE-276 synthesized in house had strong resistance against cracking under solution stressing since none of the specimens tested had failed during the course of the ESCR experiments. This is probably due to relatively higher molecular weight values and less percentage of chain branching as indicated in Table **1**. Both homemade synthesized polyethylene, *i.e*. HDPE-276-30 and HDPE-276-40, showed excellent resistance to stress cracking in the presence of chemical solution as this was clearly demonstrated by the stressed samples (Figure **3**). All tested samples of HDPE-276 appeared to be free of crack propagation or splitting. In contrary,

Table 1: HDPEs Used in this Study

Melt Flow Index, MFI (g/10 min) @ 2.16 kg and 190 °C	Branches/end Group %	Molecular Weight /1000 (g/mol)	Polymerization Parameters	Polymer
No flow	0.04	696	30 par, 24 °C	HDPE-276
No flow	0.02	610	40 par, 24 °C	HDPE-276
0.107	-	-	-	HDPE-C

Table 2: ESC Behavior of Homemade and Commercial HDPE

Observation Time (hr)	# Failed Samples				
	HDPE-C in Solution	HDPE-C in Water	HDPE-C w/o Solution	HDPE-276-30	HDPE-276-40
0.1	0	0	0	0	0
0.25	0	0	0	0	0
0.50	0	0	0	0	0
1	0	0	0	0	0
1.30	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
6	2	0	0	0	0
8	5	0	0	0	0
16	10	3	0	0	0
24	A	7	0	0	0
32		10	0	0	0
40		A	2	0	0
48			5	0	0

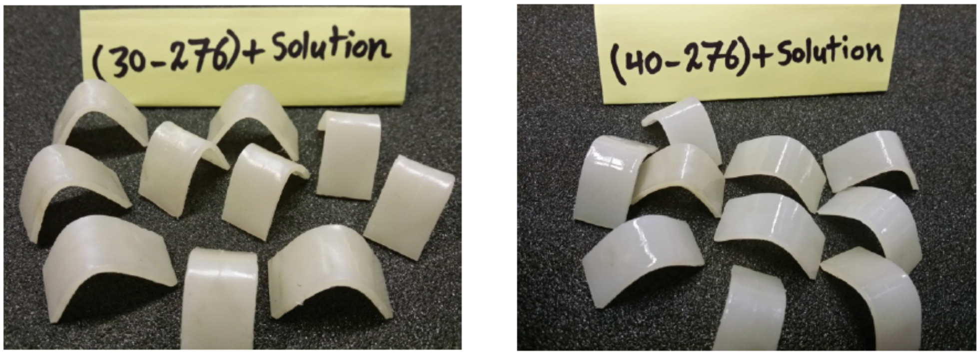

Figure 3: Appearance of homemade HDPE (HDPE-276-30 and HDPE-276-40) after the course of ESCR test.

a commercial HDPE (HDPE-C) stressed under the solution started to crack after 4 hours of testing and reached maximum number of failed samples at about 20 hours of testing as shown in Table **2** and Figure **4**. HDPE-C was also tested without applying any solution and surprisingly was found to be susceptible to dry environmental stress cracking as illustrated in Figure **5**.

This was also true when replacing IGEPAL solution with ordinary water were one can see that samples of HDPE-C may be cracked and ultimately splitted when stressed in the presence of water (Figure **6**). This comparison study emphasizes the importance of selecting proper grade of PE for harsh environment of stresses both dry and solution even when the liquid is ordinary water. Recall that HDPE-C is a commercial one where additives are involved and that might have an effect on the ESCR. HDPE-276 is a natural one, *i.e*. only contained PE and traces of catalysts with no additives or fillers.

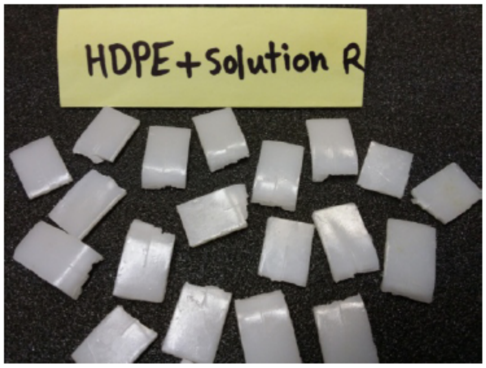

Figure 4: Cracking of all samples of commercial HDPE (HDPE-C) after the course of ESCR test.

Figure 5: Cracking of some of the samples of commercial HDPE (HDPE-C) after the course of ESCR test without using any solution.

Figure 6: Cracking of the samples of commercial HDPE (HDPE-C) after the course of ESCR test with water.

CONCLUDING REMARKS

This study highlighted the importance of selecting proper type of PE for harsh application when the material is subjected to stresses not only when dealing with solutions but also when handling ordinary water. Potential applications are liquid transfer through PE pipes and lining for landfills. Another factor that might have an effect on ESCR of PE is amount and type of additives and fillers used when manufacturing PE.

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