KFUPM
Chemistry Department
CHEM 399

Polyethylene Quality Assurance Tests in Petrokemya

Report of Summer Training 063

Summer Training Coordinator

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I- Introduction.

a- Petrokemya in Summary

Arabian Petrochemical Company referred to as "PETROKEMYA" is wholly owned by Saudi Basic Industries Corporation "SABIC". It was established in May 1981 at JUBAIL Industrial City to construct and operate petrochemical complex. PETROKEMYA currently consist of the following plants:

Table 1

Plant	Product	Designed Capacity (MTPY)
OLEFINS-I	Ethylene	650,000
	Butene-1 Plant1	50,000
	Butene-1 Plant2	50,000
OLEFINS-II	Ethylene	800,000
	Propylene	325,000
	Butadiene	130,000
	Benzene	125,000
OLEFINS-III	Ethylene	800,000
	Propylene	360,000
	Benzene	130,000
	Butene-1 Plant 3	130,000
POLYSTYRENE	HIPS	65,000
	GPPS	50,000
	EPS	25,000
POLYETHYLENE	LLDPE HDPE	800,000
VCM	(Vinyl Chloride Monomer)	390,000
S-PVC	(Suspension Polyvinyl Chloride)	380,000
E-PVC	Paste Resin	24,000

Eastern Petrochemical Company (SHARQ), which is an affiliate of SABIC, has an ownership interest in the Ethylene plant and Olefins complexes for uplifting Ethylene, while PETROKEMYA has 50% ownership interest in SHARQ Ethylene Glycol Plants 1,2 and 3 for uplifting Glycols. In addition, Saudi European Co. (IBN-ZAHR) and Al-JUBAIL Fertilizer Co. (Al-Bayroni), both SABIC affiliates, have off-take rights in the Olefins Complexes of PETROKEMYA for uplifting Propylene.

Scope of Company Activities

PETROKEMYA prime activity is to produce petrochemicals and polymer resins for sale thru SBU's "Strategic Business Units", to customers in the Kingdom and for export to other countries worldwide. This prime activity is supported by the necessary auxiliary functions such as Laboratory, Maintenance, Industrial Safety, Security & Environmental, Planning, Quality Department and in-plant Clinic. For other support services (Accounting, Human Resources, Information Technology, Procurement, General Services and Engineering), it is provided through service agreement with Sabic Shared Services.

Main Products

Ethylene
Butene-1
Propylene
1,3 Butadiene
Benzene

Polystyrene products, GPPS, HIPS & EPS (i.e. General Purpose Polystyrene, High Impact Polystyrene and Expandable Polystyrene respectively) of different grades.

Vinyl Chloride Monomer (VCM)
Suspension Polyvinyl Chloride (S-PVC) of different grades.
Emulsion (Paste Resin) Polyvinyl Chloride (E-PVC) of different grades.
Polyethylene (LLDPE & HDPE).

Hydrogen which is by-product of Ethylene plant is sold to neighboring plants. The necessary raw materials are bought through SABIC SBU's, from neighboring SABIC affiliate companies, or directly from SAUDI ARAMCO. These are listed below:

Table 2

Raw Materials	For the Plant	Supplied By
Ethane, Propane & NG	Olefins-I / Olefins-II / Olefins-III	SAUDI ARAMCO
Styrene Monomer	Polystyrene	SADAF
Ethylene Dichloride and Caustic Soda	VCM	SADAF

PETROKEMYA also produces the utilities such as Steam, De-mineralized Water, Plant and Instrument air for distribution throughout the site. The utilities procured by PETROKEMYA are as follows:

Electricity from Saudi Electricity Company
Butene-1
Natural Gas from SAUDI ARAMCO
Nitrogen from National Industrial Gases Co.
Water from MARAFIQ.

Other chemicals, additives, catalysts required for the plant and lab chemicals needed for testing purpose, are bought through SABIC Shared Services from either in-Kingdom sources or imported from other countries. Solid and liquid wastes are disposed from the site, meeting Royal Commission's environmental standards and requirements[1].

b- Quality Assurance Department in Summary.

The Quality Assurance department's vision is to provide continuous (uninterrupted) analytical support to all Petrokemya plants through on line analyzers / or off line analyzers in a professional manner and ensure the quality of final products. Its mission is to provide analytical & technical support to all Petrokemya plants, ensure the quality of the final products, environmental, industrial hygiene and Lube Oil Monitoring. QAD areas are divided into four areas, Olefins (Carbohydrons) area, VCM (Vinyl Chloride Monomer) area, PVC (Polyvinyl Chloride) area and Polyethylene area[2]. This report will talk about the Polyethylene are in specific.

[1] http://petrokemyaweb.sabic.com/Profile/Pages/default.aspx
[2] http://petrokemyaweb.sabic.com/sites/Departments/QA/default.aspx

c- Polyethylene Section.

The Polyethylene labs consist of the following:

1- Catalyst Lab with following equipment:
XRF for testing Catalyst samples and some of the product additives

2- Rheology Lab with following equipment:
Melt Indexers and other equipment

3- Physical Testing Lab with following equipment:
FTIR for additives measuring, Color measuring equipment,
Density measuring equipment

And provide Analytical Support to PE Plant

The Polyethylene application labs consist of the following:

1- Cast Film producing machines for Gels content, Additives &
Density Testing.

2- Hydraulic Press Machines for sample specimen preparation for the physical Testing

3- Ash testing equipment

Plus other Testing Equipment[3]

[3] http://petrokemyaweb.sabic.com/sites/Departments/QA/Overview/Forms/Overview.aspx

II- Polyethylene.

Polyethylene (IUPAC name polyethene) is a thermoplastic commodity heavily used in consumer products. Over 60 million tons of the material are produced worldwide every year. Polyethylene is a polymer consisting of long chains of the monomer ethylene (IUPAC name ethene). The recommended scientific name 'polyethene' is systematically derived from the scientific name of the monomer. In certain circumstances it is useful to use a structure–based nomenclature. In such cases IUPAC recommends poly(methylene). The difference is due to the 'opening up' of the monomer's double bond upon polymerization.

In the polymer industry the name is sometimes shortened to PE, in a manner similar to that by which other polymers like polypropylene and polystyrene are shortened to PP and PS, respectively. In the United Kingdom the polymer is commonly called polythene, although this is not recognized scientifically.

The ethene molecule (known almost universally by its common name ethylene), C_2H_4 is $CH_2{=}CH_2$, Two CH_2 groups connected by a double bond, thus:

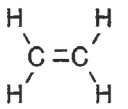

Figure 1

Figure 2

Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene[4].

Petrokemya produces two main types of Polyethylene: High Density Polyethylene (HDPE) and Linear Low Density Polyethylene (LLDPE) as Pellets (particles of ~3mm diameter) and granule (particles of ~.1mm diameter). HDPE and LLDPE densities are $\geq$0.941 g/cm^3 and ~0.915-0.925 g/cm^3 respectively. Most of the tests are applicable for both of the types.

a- Additives of Polyethylene

Primary Anti-Oxidant.

1. Irg. 1076
2. Irg. 1010

Secondary Anti-Oxidant.

Weston-399

Neutralizer.

1. Zn Stearate
2. Ca Stearate

Slip Agent

Eurcamide

Anti-Block Agent.

China Clay

b- Grades of Polyethylene and their applications:

Linear Low Density Poly ethylene (LLDPE)

1. 118N	film application
2. 118W	film application
3. 218W	film application
4. 318B	film application

High Density Poly ethylene (HDPE)

1. F00952	film application
2. F00952EQ	film application
3. F01552	film application
4. BM1052	blow molding application

c- Applications of Polyethylene:

Blow Film
LLDPE, HDPE

Cast Film
LLDPE

Blow Molding
HDPE

d- Tests of Polyethylene:

There are many different tests to determine certain properties of the product. Some of these tests are applied daily and some are applied weekly.

Melt index (MI): the measure of the rate of extrusion of a thermoplastic through a orifice of a specified length and diameter under specified condition of temperature and pressure. It's an indicator of molecular weight. This test is applied several times a day. For each batch, this test has to be applied. **(Trained to do this test)**

Melt flow ratio (MFR): this is a calculated. It is the melt flow index divided by the melt index. It is an indicator of the molecular weight distribution. This test is done infrequently if there was a demand to do it. **(Trained to do this test)**

Density: measured by the weight per unit volume. It is an indicator of crystallinity of the polymer. This test is applied several times a day. For each batch, this test has to be applied. **(Trained to do this test)**

Ash: determines the inorganic ash content of polyethylene by burning off the polymer portion. This test is applied for the general batches only.

Bulk density: the measure of weight per unit volume. Bed fluidization and conveying is affected by this variable.

Contamination: the measure of contamination caused by oxidized resin, external contamination, dirt, metal, etc. it's determined by size and number of contaminations.

Pellet Uniformity: this is a visual inspection to check the pellet are reasonably uniform in size to minimize problems in extrusion at the customer location.

Hexane extractable: the measure of low molecular weight polyethylene (oligimers) in resin used for food applications. It's required for compliance with FDA. Extractable limits apply to base resin without additives.

Color: this is a measure of what is physically acceptable to the customer. It can be dependent upon the level of catalyst residue in granular resin. This test is applied several times a day. For each batch, this test has to be applied. **(Trained to do this test)**

Additives content: this is a measure of the amount of stabilizers being added to the resin. Additives are used to prevent oxidation, act as UV stabilizer, or can be used as processing aids, or property enhancers. This test is applied several times a day. For each batch, this test has to be applied. **(Trained to do this test)**

Fan: this is a measure of gels of imperfections in the product. It is done to predict its fabrication and its aesthetic value. Gels can be either polymeric, high

molecular weight polymers or residual catalyst. This test is applied several times a day. For each batch, this test has to be applied. **(Trained to do this test)**

III- Case Studies.

I was assigned to several case studies and given the materials to carry them out. The results were then submitted to the supervisor.

a- Flow index(FI) and melt index(MI)

This case study was carried out in order to determine the most accurate results of product. The material used was SPC LLDPE and SPC HDPE.

Table 3(Pellets only)

LLDPE MI				HDPE FI			
run	mass (g)	MI (g/10min)	notes	run	mass (g)	FI (g/10min)	notes
1	2.79	1.14		1	3.98	15.42	
2	2.79	1.13		2	4.05	15.59	
3	2.74	1.16		3	4.03	15.42	
4	2.72	1.17		4	4	15.11	poured carefully
5	2.75	1.15		5	4.02	15.42	poured cont.ly
6	2.81	1.17		6	4	15.27	carefully and cont.ly
7	2.77	1.16		7	4	15.75	not cleaned
8	2.74	1.16	not cleaned	8	4.01	16.09	not cleaned
9	2.85	1.16	not cleaned	9	4	15.59	
10				10	4	15.67	
average	2.773333	1.155556		average	4.009	15.533	
Actual value		1.12				15.22	
STDEV	0.040927	0.013333		STDEV	0.019692	0.272643	due to more experiments

b- Flow index(FI) and melt index(MI) of Pellets and Granule

This case study was carried out to determine the most accurate product. The materials used are HDPE and LLDPE of pellets and granule forms of the same grade.

Table 4(Pellets and granule)

Run	low plts	low grnl	hi plts	hi grnl
1	1.82	1.98	10.18	10.04
2	1.79	1.99	10.25	10.46
3	1.77	2.06	10.18	10.02
4	1.82			10.25
STDEV	0.024495	0.043589	0.040415	0.2064582

From these two study cases, the following notes were concluded:

1- Between LLDPE and HDPE, LLDPE shows more accuracy.
2- Between pellets and granule, pellets show more accuracy.
3- Reasons of error are:
    a- The device can be easily disturbed by external vibrations.

b- The mixing of granule with IRG tolerates from time to time (inaccurate)
c- The additives in pellets form enhance uniformity of particles thus accuracy.
d- Air bubbles cause false reading and minimize accuracy.

c- Melt flow ratio (MFR):

The purpose of this study case is to determine the accuracy time consumed differences between MFR5 and MFR2 for HDPE BM1052 grade (Pellet)

MI5

weight taken	MI
2.5	0.43
2.5	0.53
2.5	0.53
2.5	0.34
2.5	0.38
average	0.442

MI21.6

weight taken	MI
3.99	8.85
3.99	8.75
3.99	8.74
3.99	8.9
4	8.87
average	8.822

MI2.16

weight taken	MI
2.01	0.07
2.01	0.07
average	0.07

MFR5 = FI/MI = MI21.6/MI5.1 = 8.82/0.44 = 20.05

MFR2 = FI/MI = MI21.6/MI2.16 = 8.82/.07 = 126

Conclusion: the results were extremely disturbed by external factors, such as temperature and contamination inside the device. Thus, the results were rejected because they were out of MFR range (22-25)

d- Trend study:

This study case was carried out to inspect the product of a certain grade throughout a period of time. The grade studied was F00952 HDPE.

Batch No.	MI	Density	Gels	Color	Irganox1010	Wenston399	ZincSt.	Calcium St.	Note
285490	9.14	0.953	0.8	-6.02	1082	1096	1133	2088	
285751	11.67	0.953	0.4	-5.91	1159	1008	1504	2022	Pre-Blend
286502	9.01	0.953	0.8	-5.87	1176	1025	1191	1931	
286675	9.41	0.953	1.2	-5.85	1336	1057	1571	2088	Pre-Blend
286950	9.29	0.954	0.2	-6.1	1015	1171	1260	2218	
287360	9.32	0.954	0.4	-6.08	1066	1188	1306	2224	
287529	9.35	0.954	0.2	-5.9	1133	1064	1470	2116	
287887	9.3	0.953	1.2	-5.99	1103	1035	1469	1978	
288002	8.83	0.953	0.4	-5.92	1063	1053	1064	1995	
288463	9.86	0.952	0.2	-6.03	1017	989	1127	1994	
288488	9.85	0.952	0.4	-6.04	1071	938	1377	1807	pre-blend
291289	8.73	0.953	0.4	-6.02	1089	943	1349	1814	pre-blend
291398	9.35	0.952	1	-5.86	986	1089	1166	1923	
291476	9.1	0.952	0.2	-5.98	1011	1162	1393	2109	pre-blend
291751	8.92	0.952	0.2	-5.96	992	1084	1238	2018	
292936	8.91	0.953	0.2	-5.94	1107	997	1470	1848	pre-blend
293081	8.79	0.952	0	-5.6	1037	985	1426	1925	pre-blend
293378	8.45	0.953	0	-5.58	1071	1011	1481	1927	pre-blend
293555	9.69	0.952	0.8	-5.43	1004	1116	1318	2048	
293976	8.53	0.953	1	-5.44	1005	1063	1245	1889	
295144	9.43	0.952	0.8	-5.75	973	1057	1278	1949	
295317	9.13	0.952	0.2	-5.73	1140	1086	1493	1873	pre-blend
295517	8.42	0.954	0.6	-5.46	1170	1001	1400	1864	pre-blend
295886	9.41	0.953	0	-5.62	1137	906	1326	1759	
Refrence values	7.0-11.0	0.950-0.954	0-4	-8.00-+3.5	1000-1600	1000-1600	1000-1500	1800-2300	

These results are collected in an ordinary way, not the inspectional way, and for that, the results tend to fluctuate from time to another. This fluctuation is due to plant issues and inspection issues. The inaccuracies of devices added to human errors create a low accuracy factors.

IV- Conclusion.

This report talked about a few case studies, Polyethylene as a product, Polyethylene section in QAD and a summary of Petrokemya of SABIC.