The Degradation of PET Resin and Generation of Acetaldehyde in PET Injection Molding Process[1]

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ABSTRACT

This research was conducted to investigate the degradation of PET resin in injection molding process and the generation of the degradation by product (acetaldehyde). Eight preform samples with different weights from different manufacturers were analyzed. Some quality control test such as moisture content analysis and intrinsic viscosity was done on the resin before production while defect check with the help of a polarizer and acetaldehyde analysis on the preform tube. Process parameters such as such as drying time, drying temperature, extruder temperature, screw rotation speed, back pressure, mold temperature, injection pressure, injection time, etc. were analyzed. The degradation in the injection molding process was classified into three groups namely, oxidative degradation which occurs during the pre-drying of the resin pellets as a result of excess oxygen attack on the polymer chain. Hydrolytic degradation occurs as a result of water molecules in the resin when subjected to high temperature and the water molecules causes' chain scission. Thermal degradation is as a result of subjection of resin pellets under high temperature with the absence of oxygen.

Keywords: *PET; Degradation; Injection molding; Preform, Intrinsic Viscosity (IV); Glass transition temperature*

INTRODUCTION

Poly (ethylene Terephthalate) (PET) is a member of the thermoplastic family. PET has a large molecular structure consisting of about 100 to 140 repeating units. PET can either be a homopolymer or a copolymer. A homopolymer is combination of monomers with one functional group while a copolymer is a combination of monomers with different functional groups.

The manufacture of PET can be described in three ways Esterification, Polymerization (Condensation) and Crystallization. First, ethylene is gotten from thermal cracking of naphtha from petroleum refining. Hydroxylation of ethylene using Potassium Permanganate as catalyst for the production of ethylene glycol (ethane-1, 2-diol). Esterification occurs between an acid and an alcohol to form an ester and a byproduct (Water). In PET production a di-acid (Terephthalate Acid) reacts with a compound with two diols (ethylene glycol) to form a polyester or a polymer. In the polymerization reaction of PET formation, the amorphous grain obtained at the polymerization process contains about 50ppm to 100ppm of acetaldehyde due to temperature and residence time used in the process. Acetaldehyde is diffused out of the resin with the glycol with the use of N_2 process also, some catalysts are used to influence the side reaction and to reduce Di (ethylene Glycol) (DEG) or Acetaldehyde. They are still present when drying or processing this may cause the preform tube or resin to turn pale yellow when over dried or oxidized. This is referred to as oxidative degradation of PET.

An injection molding machine is used for the production of PET preform tube. It has high efficiency and manufacturability. In the machine we have the extrusion process where the dried resin pellet from the dryer is melted

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into a polymer melt with the help of the heater band and the screw. Injection process, the injection plunger is used to inject the molten plastic into the cavities through the hot runner with a very high pressure and the molding process commences. In the molding process there are several stages like fast fill, transition, hold and cooling stage. These molding stages form the injection cycle. The combination of these processes bring about the manufacture of the preform tube.

Due to the hygroscopic nature of PET resin, high moisture content or acid/alkaline impurities can lead to degradation and excessive loss in mechanical strength or Intrinsic Viscosity during plasticizing if not properly dried. Well, this is known as Hydrolytic Degradation of PET. The rate of hydrolysis is determined by the nature of its chain end. Increase in the carboxyl end group will increase the rate of hydrolysis [3].

Heating of PET resin above the melting point in the barrel or mold as a result of high temperature from the heaters or as a result shear heat can break chemical compounds in PET resin which will result to the generation of Di (ethylene Glycol). This degradation is referred to as Thermolysis or Thermal degradation of PET [6].

Degradation is chemical process which affects the mechanical, physical and chemical properties of that compound. These properties affected can be the color, chemical bond, mechanical strength, etc. The effect of environmental factors on a polymer over a period of time can lead to the disintegration of the polymer structure. In the degradation of PET, the polymer chain is regenerated and a certain degree of polymerization is maintained. This result to the displacement of hydroxyl end groups by carboxylic acid end groups, acetaldehyde production is equivalent to this process.

Acetaldehyde is an organic chemical compound which belongs to the aldehydes family. Its chemical formula CH_3CHO. It's found naturally in ripe fruits, coffee, bread and it's produced by plants [5]. It's also produced from the partial oxidation of ethanol by the liver enzyme alcohol dehydrogenase and it usually result to hangover after alcohol consumption. High consumption of disulfiram inhibits the enzymatic actives of dehydrogenase in breaking down of acetaldehyde and this will lead to accumulation of acetaldehyde.

Also, when PET resin is heated above its temperature to produce preform tubes or bottles acetaldehyde is produced as a by-product. A little quantity of acetaldehyde which is harmless to the human body may migrate from the preform tubes or bottles to the beverage stored in the bottle. The consumer may be able to detect the taste when the acetaldehyde concentration is above 0.025mg or 3ppm of AA. This is mostly observed in water bottles due to the tasteless and odorless qualities.

MATERIALS AND METHODS

MATERIALS

The materials used for this experiment are as follows eight preform tubes and PET resin samples of different weight and manufacturers, an Acetaldehyde analyzer (PIOVAN) and an injection molding machine (Husky HYPET 500). All experiment was conducted at the Nigeria Bottling Company, Benin Plant.

METHODS

As soon as the samples (preform tubes) arrived at the lab, it was stored in a cool and dry place of about $16^{O}C$. The preform samples were grouped by their weights and the time of production. The resin was stored in a cool and dried place to avoid contact with atmospheric moisture. It was grouped and gotten from different manufacturers. A data sheet was compiled for these information

8 samples (preform tubes) of different weight were collected. 2 samples of 24.7g CSD preform tubes, 2 samples of 22.4g CSD preform tubes, 2 samples of 17g water preform tubes and 2 samples 28g of water preform tubes were collected from a producer. Also, 10g of resin pellets for CSD and water from different producers were collected. A quality control test is usually carried out on the resin pellets. Various test like moisture content analysis and intrinsic viscosity was carried out. The results from this tests determines the parameters for the injection molding process.

A moisture content analyzer which uses the principle of Loss on Drying (LOD) was used to check the amount of moisture content in the resin pellets. The resin pellets are placed on a tray inside the machine where it measures the weight of the resin before and after heating. This will help us determine our drying temperature set point.

A close observation was done at the injection molding process machine optimized parameters determined from the quality control tests of the resin pellets, where the preform tubes were produced. Optimized parameters like the Residence drying time, the barrel (extruder) temperature, and mold temperature, fast fill time, transition time, hold time, hold pressure and cooling time. Data was collected and grouped by sample weights and the resin types based on the manufacturers.

Acetaldehyde test was carried out 24hours after production. A PIOVAN (Inspecta) acetaldehyde analyzer which uses a hydrogen generator was used to analyze the preform sample. The analyzer uses gas chromatography technology with five automatic phases involved in the determination of acetaldehyde content in the preform: washing, sample conditioning, load of the loop and gas chromatographic analysis. The polymer (preform tube) was kept in a headspace where it was washed, sampled by its weight, resin type, etc. and heated to about 130^{O}C. The hydrogen gas which was generated by the hydrogen generator with the use of electrolysis serves as the carrier gas. It carries acetaldehyde from the heated preform tube. The weight of the acetaldehyde is then analyzed in the result. The Acetaldehyde results were recorded by the preform weights, preform type and the resin type.

DISCUSSION

In injection molding process there are different areas in the injection molding machine where PET resin degrades and acetaldehyde is generated but note that there is a specific amount of acetaldehyde in the resin pellets. This is based on consumer's specification.

The preform samples were grouped by the types of resin from different manufacturers, the preform types and their weights.

Table 1. Preform tube samples analysis

Sample Name	Sample Weight (g)	Sample Type	Resin Type	Resin Moisture Content Before Production (%)	Acetaldehyde content of the resin (µg/g)
22.4A	22.4	CSD	Ramapet S1	0.025	0.71
22.4B	22.4	CSD	Hanian Yisheng	0.021	0.72
24.74A	24.74	CSD	Ramapet S1	0.029	0.86
24.74B	24.74	CSD	Hanian Yisheng	0.022	0.68
17A	17	Water	Ramapet N1	0.025	0.83
17B	17	Water	Engee 2.0	0.026	0.77
28A	28	Water	Ramapet N1	0.023	0.69
28B	28	Water	Engee 2.0	0.021	0.82

Table 1 shows the analysis of the 8 preform tube samples which was collected and classified by their weight, their sample type or the use of the preform tube like CSD (Carbonated Soft Drink) and water also, classified by the type or resin from different manufacturers also the moisture content analysis result. The resin type also depends on the use of the preform tube like Ramapet S1 and Hanian Yisheng which are used for CSD preforms while Ramapet N1 and Engee 2.0 are used for water preforms.

The amount of moisture content in the resin pellets determines the pre-drying residence time and the pre-drying temperature. If not properly dried in the dryer hopper it will lead to hydrolytic degradation of the resin pellets which generates high acetaldehyde content as a by-product and results to low IV of the resin pellets. Hydrolytic degradation happens when PET resin with moisture content is heated above its glass transition temperature (T_g) which is usually between 67ºC to 80ºC (due to the semi crystalline nature of PET). The pre-drying of PET resin is done to achieve dew point of -30ºC to -45ºC and to eliminate moisture content in the resin pellets. Sample 24.74A as a case study, whose moisture content analysis was 0.029% before production. The set point for the drying temperature and dew point was recorded to be was 171ºC and -27ºC respectively, for a residence time of 6hours. The average barrel temperature (feed zone temperature) when the resin pellet entered was recorded to be 297ºC. The high barrel temperature which is above the T_g is due to the high IV loss resulting to loss in the mechanical properties of the resin. This effect will make the screw rotation faster due to low mechanical strength of the resin pellets resulting to low shear force. This will make the viscosity of the melt low and result to possible defects like short shot, high acetaldehyde and haziness in the preform. The result of the acetaldehyde analysis of sample 24.74A was high as a result of the hydrolytic degradation from figure 1.0. Chemically, it's assumed that amorphous regions of PET resin accommodate the diffusion of water where hydrolysis occurs at a rate which also depends on the relative humidity, temperature, shape and degree of crystallinity. [1, 4]

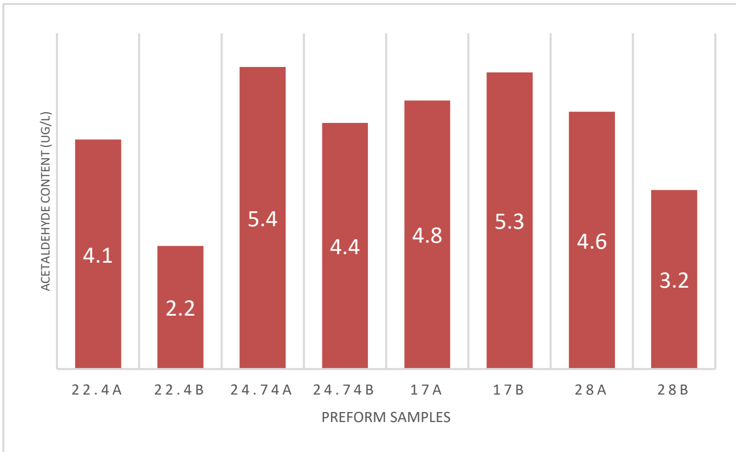
Sample Name	Injection Molding Process Optimized Parameter										
	Drying Time	Drying Temperature (°C)	Dew Point (°C)	Highest Extruder Temperature (°C)	Screw Back Pressure (Bar)	Average Mold Temperature (°C)	Injection Time (S)	Injection Pressure (Bar)	Hold time (S)	Hold Pressure	Cooling Time (S)
22.4A	6 Hours	170	-40	294	60	280	1.54	1250.8	3.0	465	2.5
22.4B		173	-38	289	62	285	1.62	1288.5	3.0	463	2.3
24.74A		171	-27	297	64	275	1.69	1087.6	3.5	375	2.7
24.74B		175	-32	286	60	280	1.67	1156.6	3.5	377	2.7
17A		181	-42	280	50	280	1.70	1200.0	3.8	402	2.8
17B		182	-47	283	55	280	1.72	1287.1	3.8	402	2.8
28A		181	-41	286	73	280	1.79	1209.7	3.8	380	3.3
28B		180	-33	296	71	280	1.77	1256.9	3.8	380	3.3

Table 2. Optimized Injection Molding Process parameters

Oxygen has a long way to play in the degradation of PET resin. Studies have shown that PET can absorb about 40-70ppm of oxygen on the polymer surface [2]. In the drying process of PET resin. Hot and purified air which its major component is oxygen is used to dry the resin pellets or to achieve a dew point 45°C. This is achieved when the right optimized drying time, drying temperature and air flow velocity is used. Earlier, we discussed the state of the PET resin when it's not properly dried as a result of either low drying residence or low drying temperature. When the drying temperature or residence time is too high this can result to destruction of the mechanical, physical and chemical properties of the PET resin. Mechanically, the resin will have excessive IV (Intrinsic Viscosity) drop. Physically, the color of the resin will change to brown of pale yellow which signifies that the resin is burnt or oxidized. Chemically, will have chain scission as a result of attack from oxygen which is also the degradation of the PET resin and the byproduct of this chain scission is acetaldehyde. This degradation is known as thermo-oxidative degradation. It's advisable to purge at least the first two shorts before activation of injection cycle to avoid defects like burnt resin, haziness, bubbles, etc. Sample 17B as a case study. The drying temperature was recorded to be 183ºC and dew point of -47. After observing our Standard Operating Procedure (SOP) of purging at least twice to avoid possible defects. We started our injection cycle and noticed a slight pale yellow preform which resulted to a high acetaldehyde after analysis. This was due to wrong drying temperature and residence time. The drying process wasn't regulated properly. If drying for a residence time of 6hours, it's advisable to set your drying temperature at 140ºC for the first 2hours, 160ºC for the next two hours and 180ºC for the last two hours.

In the mold and runner PET resin is subjected to high temperature in the absence of oxygen the polymer properties changes and there is excessive loss of molecular weight, this is known as thermal degradation of the resin. This degradation occurs in the hot runner where polymer melt passes through before entering the cavities. The high temperature might be as a result of wrong process parameters or wrong material specification (intrinsic viscosity). The wrong process parameters may include high mold temperature or high injection pressure. Injection pressure is in two phase, the fast fill and the transition. The injection pressure is as a result of how hard the machine pushes the resin to the cavities and the resistance of the resin.

Fig 1.0 Graphical Analysis of the amount of Acetaldehyde in the various PET preform tubes samples



The fast fill is when the polymer melt forms the body of the preform, this is done with a high injection pressure while transition is when the neck finish is formed the injection temperature is reduced so the flow won't be disturbed. If excessively hot melt is injected to the cavity. The flow properties will be affected which will cause a longitudinal or hooked silvery white streaks on the preform tube. This defect is known as splay. Also, there will be loss in molecular weight as a result of chain scission in the polymer chain or degradation and generation of acetaldehyde as byproduct from the degradation process. The loss in molecular weight as a result of high temperature can reduce the viscous content of the melt which will lead to possible defect like short shot, the short shot defect will make the preform weight less and incomplete formation of the preform tube. The low viscous melt increases the injection pressure due to low resistance from the melt.

CONCLUSION

We can conclude that degradation in PET injection molding process depends on the process control which involves the temperature and pressure control. Also the material specification like intrinsic viscosity is a key factor in the optimization of the injection molding parameters.
We also observed that the degradation process in various part of the injection molding machine is accompanied with defects like high acetaldehyde, haziness, burnt preform, short shot and splay.

Acetaldehyde can also be formed when the preform tubes is stored in an unfavorable environment and also during stretch blowing of the preform tube.

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