EFFECTS OF SOLVENT COMPOSITION AND POLYMER CONCENTRATION ON POLY (ETHYLENE TEREPHTHALATE) DEGRADATION IN PHENOL: 1, 2-DICHLOROBENZENE BLENDED SOLVENT.

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ABSTRACT

Poly (ethylene terephthalate) was evaluated for its acid number, ash content and melting temperature, and were found to be 2m mol COOH/Kg, 0.0037% and 260-263^{0}C respectively. Its solution in Phenol: 1,2-dichlorobenzene solvent mixtures of 35%: 65%, 50%: 50%, 65%: 35% by weight was degraded at 143± 2°C. The effects of solvent composition and polymer concentration on poly (ethylene terephthalate) degradation in solution were investigated by dilute solution viscometric method using 0.460, 0.500 and 0.540 g/dl polymer concentrations, respectively. Results indicate that at 35%: 65%: by weight Phenol: 1,2-dichlorobenzene solvent composition, intrinsic viscosity–degradation time profile was linear with slopes of 2.50×10^{-4}, 3.10×10^{-4} and 3.33×10^{-4} and $dlg^{-1}min^{-1}$ for polymer concentrations of 0.460, 0.500 and 0.540 g/dl respectively.
This showed that the rate of degradation increased with increase in polymer concentration. Similar results were obtained for 50% Phenol: 50% 1,2-dichlorobenzene solvent mixture but with an initial high rate of degradation within the first 60 minutes of degradation time. At 65% phenol concentration, a decrease in the rate of degradation as the polymer concentration increased was observed as evidenced by a decrease in the slopes of the linear plots from $3.06 \times 10^{-4} dlg^{-1} min^{-1}$ to $2.63 \times 10^{-4} dlg^{-1} min^{-1}$ for a decrease in polymer concentration from 0.500 g/dl to 0.460g/dl.

KEYWORDS: Poly (ethylene terephthalate), Degradation, Solution Viscometry.

INTRODUCTION

Poly (ethylene terephthalate) (PET) (Fig.1), is formed by the condensation of terephthalic acid or its dimethyl ester with glycol. Poly (ethylene terephthalate) is only one representative of a substantial class of polymers known as polyesters. It is linear and therefore, thermoplastic with a melting point range of 260-270°C. Properties and performance of poly (ethylene terephthalate) have been reported (Fuller, 1940; Bunn, 1953).

Bulk undissolved poly (ethylene terephthalate) is known to degrade within the temperature range of 300-500°C (Allcock and Lampe, 1981), yielding mainly oxygen – containing compounds, such as, carbon dioxide, acetaldehyde and terephthalic acid as products (Masuda et al, 1996). The decomposition of poly (ethylene terephthalate) to its monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG) by solvolysis (methanolysis) in supercritical methanol has been reported (Goto et al, 2000). A number of studies on the degradation of poly (ethylene terephthalate) have been reported (Gubanski and Montanari, 1992; Szczepanowska and Wilson, 2000; Song et al, 2002; Dhavalikar, 2003).

Polymer solutions are primarily useful as viscosity control agents. One of the striking non-equilibrium properties of a long chain-like molecule is its ability, when dissolved at very low concentration, to alter the flow properties of the mixture. The quantitative determination of this effect on solution flow at low polymer concentration is termed dilute solution viscometry. Attention has been drawn to the utility of viscosity measurements on dilute solutions as a means of polymer characterisation (Staudinger and Heuer, 1930). A number of factors affect the breakdown in viscosity especially in its application as agent for controlling viscosity.

Information on the effects of solvent composition and polymer concentration on poly (ethylene terephthalate) degradation in solution is scanty. This paper describes the effects of solvent composition and polymer concentration on the degradation of poly (ethylene terephthalate) in blended phenol: 1,2-dichloro benzene solvent.

EXPERIMENTAL
MATERIALS

Poly (ethylene terephthalate) chips (Lucky Polymers), were obtained from Horizon Fibres, Port Harcourt. They were transparent and colourless tiny chips of 0.5 mm diameter and 3 mm in length. They were dried in a Heraeus vacuum oven (105°C) and at a pressure of 200 millibar for 3 hours. 99 % phenol crystals (May and Baker), 1,2-dichlorobenzene was obtained from Riedel de Haen and was of analytical reagent (b.p. 178-180 °C). All other chemicals used were of laboratory reagent.
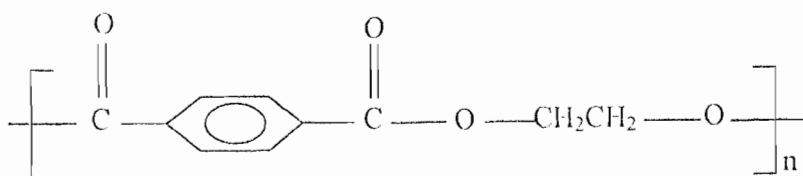
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Fig. 1: Poly (ethylene terephthalate)

METHOD

Preparation of Solvent Mixture

1000g phenol crystals were placed in a "Memert" oven for 5 hours at 60°C to ensure minimal generation of toxic phenolic vapours. Equal weights of the molten phenol and 1,2-dichlorobenzene were then mixed together in a Winchester bottle. The bottle was corked and the warm mixture was shaken using an electronic shaker at the rate of 160-172 revolutions per minute (rpm) for 1.5 hours. The solvent mixture was finally allowed to cool to room temperature. This gave 50%: 50% by weight mixture of phenol and 1,2-dichlorobenzene. The procedure was repeated to obtain 35%: 65% and 65%: 35% by weight mixtures of phenol: 1,2-dichlorobenzene respectively.

Preparation of Polymer Solution

1.15g, 1.25g and 1.35g predetermined weights of poly (ethylene terephthalate) chips were introduced into 3 x 100 ml volumetric flasks, and 50 ml of the prepared solvent mixture were next added respectively. These mixtures were heated to 143±2°C over a silicon oil bath using multi temperature thermostatically controlled electric heater. The flasks and other contents were shaken at 150 rpm until complete dissolution took place.

Determination of Melting Temperature of Poly (ethylene terephthalate) Chips

This was accomplished according to standard procedure (Lurgi, 1988).

Determination of Ash Content

3.0g Poly (ethylene terephthalate) was accurately weighed unto a dry crucible of known weight. The crucible containing the polymer was then allowed to ash using the rapid incinerator at 800°C for 45 minutes. The left over (small whitish inorganic matter) in the crucible was allowed to cool to room temperature in a desicator and weighed. The percent ash content was calculated using the following equation:

$$\text{Ash content (\%)} = \frac{\text{Sample end weight}}{\text{Sample initial weight}} \times \frac{100}{1} \quad \text{... (1)}$$

Determination of Acid Number (Free Carboxyl Group)

4.0g poly (ethylene terephthalate) was accurately weighed into a 250 ml round bottomed flask and to which 3 pieces of glass beads were added. 70g of 2:3 ratio of phenol: chloroform was added into the flask and then refluxed for one hour. 0.5 ml of 0.1%

tetrabromophenol blue solution was added with constant shaking to the resulting cooled solution, which turned yellow. The yellow solution was then titrated with 0.1 M potassium hydroxide solution in benzyl alcohol. A colour change to blue via an intermediate green colour signified the end point. A blank titration was next carried out under the same conditions. The acid number was calculated using the following equation:

$$\text{Acid number (mmol COOH/Kg PET} = \frac{(A - B) \times F}{E} \times \frac{0.1}{1} \times \frac{100}{1} \quad \text{... (2)}$$

Where, A = volume of the 0.1M KOH solution for sample titration (ml)

B = volume of the 0.1M KOH solution for blank titration (ml)

F = factor of the 0.1M KOH solution

E = weight of poly (ethylene terephthalate) (g)

Determination of the Factor (F) of the 0.1M KOH Solution

0.122g benzoic acid was accurately weighed into a 250 ml round bottomed flask and 50 ml ethanol, plus 3 drops of 0.1% phenolphthalein solution were next added. This mixture was then titrated with the 0.1M KOH benzyl alcohol solution until the colour became pink. A blank (without benzoic acid) titration was also carried out. The Factor (F) was calculated using the following equation.

$$\text{Factor (F)} = \frac{10 \, (\text{ml})}{(A - B) \, \text{ml}} \quad \text{.......(3)}$$

Where, A = volume of 0.1M KOH solution for sample titration (ml)

B = volume of 0.1M KOH solution for blank titration (ml)

Viscosity Measurements

Viscosity measurements were carried out according to standard procedure (DIN, 1985) using a mixture of phenol / 1,2-dichlorobenzene as solvent at 25°C. 1.15g, 1.25g and 1.35g pre-determined weights of poly (ethylene terephthalate) chips were introduced into a 3x100ml volumetric flasks and 50 ml of the prepared solvent mixture of different compositions 35%: 65%, 50%: 50% and 65%: 35% by weight of phenol: 1,2-dichlorobenzene, described in section 2.2.1 were then added to prepare solution A, which were allowed to cool to room temperature. These were then placed in a hot temperature oil bath (143±2°C) equipped with electric shaker, which was maintained at a constant rate of

Table 1: Efflux Time Values for Poly (ethylene terephthalate) Solution in 35% phenol: 65% 1,2-dichlorobenzene Solvent Mixture at 25°C.

Conc. of PET(g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.460	70.010	94.530	94.007	93.414	92.827	91.757	91.197
0.500	70.010	96.150	96.327	95.213	94.917	93.633	92.930
0.540	70.010	99.623	98.517	97.723	96.690	95.483	94.793

Table 2: Efflux Time Values for Poly (ethylene terephthalate) Solution in 50% phenol: 50% 1,2-dichlorobenzene Solvent Mixture at 25°C.

Conc. of PET(g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.460	92.133	124.367	123.340	122.347	122.347	121.533	120.780
0.500	92.133	128.030	125.537	124.837	124.290	123.780	123.143
0.540	95.843	135.377	133.543	132.560	131.107	130.683	129.533

Table 3: Efflux Time Values for Poly (ethylene terephthalate) Solution in 65% phenol: 35% 1,2-dichlorobenzene Solvent Mixture at 25°C .

Conc. of PET(g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.460	129.707	127.305	169.290	168.450	167.433	165.410	163.840
0.500	129.707	174.500	172.765	171.970	170.435	168.400	167.635
0.540	129.707	180.100	174.297	173.875	173.243	170.350	167.890

150 rpm. The process was allowed to continue for another 5 hours and at 1hr intervals, 10 ml of the solution was withdrawn with a pipette into a 50ml volumetric flask and the mark made up with a mixture of phenol/ 1,2-dichlorobenzene (pure solvent) to obtain solution B. The concentration of the resulting solution B was calculated using the following equation:

$$X = \frac{10\,(ml) \times A}{50\,(ml)} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Where, X = concentration of solution B (g/50ml)
A = weight of PET used in preparing solution A (g)

Solution B was used for viscosity measurements for times (degradation times) corresponding to 60, 120, 180, 240, 300 and initial reading of 0 minutes respectively. Results of the efflux times of solutions and solvents are shown in Tables 1–3. Relative viscosities. (η_{rel}) were calculated using Eq. 5

$$\eta_{rel} = \frac{t}{t_0} \quad \ldots\ldots\ldots\ldots (5)$$

Where, t = efflux time of solution
t_0 = efflux time of solvent

Intrinsic viscosities [η] were determined from a standard graph, which relates relative viscosities with intrinsic viscosities for poly (ethylene terephthalate) dilute solution in phenol/ 1,2-dichlorobenzene solvent mixtures (DIN,1985). Results are shown in tables 4-6.

RESULTS AND DISCUSSION

Characterisation of Poly (ethylene terephthalate)

Poly (ethylene terephthalate), (PET) chips used in this study were characterised by determining their melting temperature, ash content and acid number respectively. The melting temperature was found to be in the range of 260 – 263 °C, which is the normal temperature range for commercial poly (ethylene terepathalate) used in melt spinning process. The melting temperature indicates a degree of polymerisation of 150 (Allcock and Lampe, 1981).

The ash content was determined in order to estimate the inorganic content of the polymer. After the ashing process, the inorganic residue was calculated to be 0.0037%. The inorganic residue may have originated from impurities in the raw materials used in the manufacture of the polymer or as a result of contamination by the reaction vessels of the manufacturing plant. It may also have resulted from the catalyst (antimony oxide, Sb_2O_3) used in the manufacture. However, the value was found to be quite low.

Acid number, a measure of the free terephthalic acid content of the polymer was determined to be 23

Table 4:
Intrinsic Viscosity Values for Poly (ethylene terephthalate) solutions in 35% phenol: 65% 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of PET(g/dl)	Intrinsic Viscosity Values (dl/g) at Various Degradation Time (min)					
	0	60	120	180	240	300
0.460	0.583	0.571	0.559	0.546	0.523	0.511
0.500	0.639	0.621	0.597	0.591	0.563	0.548
0.540	0.691	0.668	0.656	0.629	0.603	0.588

Table 5: Intrinsic Viscosity Values for Poly (ethylene terephthalate) Solutions in 50% phenol: 50% 1,2-dichlorobenzene Solvent Mixture at 25°C.

Conc. of PET(g/dl)	Intrinsic Viscosity Values (dl/g) at Various Degradation Time (min)					
	0	60	120	180	240	300
0.460	0.582	0.566	0.555	0.549	0.536	0.524
0.500	0.642	0.601	0.590	0.581	0.573	0.562
0.540	0.676	0.648	0.632	0.609	0.602	0.585

Table 6:
Intrinsic Viscosity Values for Poly (ethylene terephthalate) Solutions in 65% phenol: 35% 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of (g/dl)	Efflux Time Values (dl/g) at Various Degradation Time (min).					
	0	60	120	180	240	300
0.460	0.550	0.515	0.506	0.493	0.470	0.452
0.500	0.575	0.555	0.546	0.529	0.505	0.496
0.540	0.640	0.573	0.568	0.560	0.527	0.499

mmol COOH / Kg PET chips. This value is acceptable in the polymer industry, particularly when the poly (ethylene terephthalate) chips are to be used for synthetic fibre manufacture (Lurgi, 1988).

Viscosity of Solvent Mixtures

Phenol: 1,2-dichlorobenzene mixtures of 35%: 65%, 50%: 50% and 65%: 35% by weight were used in this study. The resulting mixtures are clear colourless and transparent. The solvent efflux time was found to increase with increasing composition of Phenol. 35% phenol gave an efflux time in the range of 70.01 to 70.20 seconds, while 50% phenol gave efflux time of 91.19 to 95.84 seconds. The 65% phenol: 35% 1,2-dichlorobenzene gave efflux time in the range of 128.56 to 129.70 seconds. These variations in efflux time of the solvent mixtures can be accounted for on the basis that 1,2-dichlorobenzene is a solvent of low viscosity and has the capacity to dissolve phenol, which is a solid at room temperature.

Thus, when phenol is mixed with 1,2-dichlorobenzene, the viscosity of resulting mixture will be higher than that of 1,2-dichlorobenzene. Similarly, as the concentration of phenol in the mixture increases, the viscosity of the solvent mixture increases accordingly.

Effects of Solvent Composition and Polymer Concentration on Poly (ethylene terephthalate) Degradation.

Efflux time and intrinsic viscosity results are shown in tables 1-3; and 4-6 respectively. Plots of intrinsic viscosity versus degradation time are shown in Figs. 2-4 for various solvent compositions. Results show a general increase in intrinsic viscosity as concentration of the polymer increases. This is due to the fact that in concentrated solution of linear polymers chain entanglement is pronounced and this in turn leads to enhanced viscosity drag due to the enlarged hydrodynamic volume of the polymer molecule.

For the plot representing 35%: 65% phenol: 1,2-dichlorobenzene solvent composition, there is a linear relationship between the intrinsic viscosity and degradation time for all the concentrations of 0.460 g/dl, 0.500 g/dl and 0.540 g/dl studied. The slopes, which show effects of concentration on the degradation of poly (ethylene terephthalate) in solution were found to be 2.50×10^{-4}, 3.10×10^{-4} and 3.33×10^{-4} dlg^{-1}min^{-1} for polymer concentrations of 0.460, 0.500 and 0.540 g/dl respectively. This shows that the rate of degradation increases with polymer concentration at this solvent composition.

This is particularly due to the fact that at high polymer concentrations more free macro radicals will be generated which initiate further degradation. Also, solvent composition is thermodynamically poor, such that molecular extension factor plays no important role in the degradation rate. This therefore accounts for the linearity of the viscosity-time profile shown in Fig. 2 for this solvent composition.

For plots representing 50% phenol: 50% 1,2-dichlorobenzene solvent compositions shown as Fig. 3, initial high degradation rate was observed (i.e. the first 60 minutes). However the intrinsic viscosity-time profile became linear after the first 60 minutes. The initial high rate of degradation could be as a result of thermodynamic solvent effect on the polymer chain. For example with increased phenol composition of the solvent, there is an increase in molecular extension of polymer chains in the solution, which means greater applied tension on the polymer molecules. This molecular extension is greatest at the initial stages of degradation when the polymer molecule or macro radicals are still long.

The slopes of the linear portion of the plots were determined to be 1.72×10^{-4}, 1.67×10^{-4} and 2.63×10^{-4} dlg^{-1}min^{-1} for polymer concentrations of 4.60, 0.500 and 0.540 g/dl respectively. Again it is observed that degradation rate increases with increase in polymer concentration, which is due to greater amount of macro radicals generated at high polymer concentrations.

The results obtained for 65% phenol: 35% 1,2-dichlorobenzene solvent composition shown as Fig. 4 show linear intrinsic viscosity-time profiles at poly (ethylene terephthalate) concentrations of 0.460 and
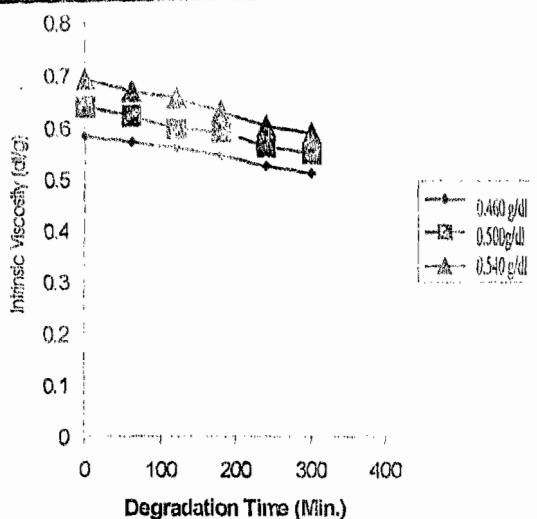
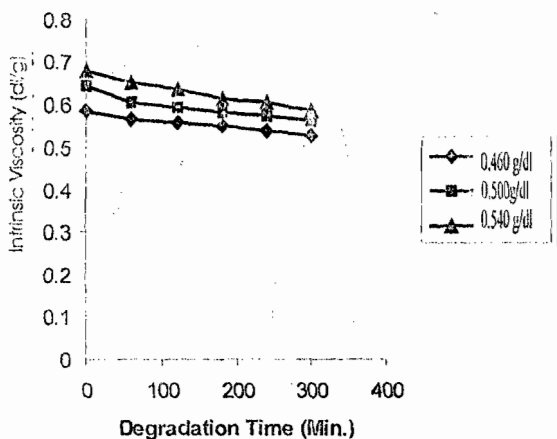Fig.2 Intrinsic Viscosity - Time Profiles for 35% Phenol:65% 1,2-Dichlorobenzene PET Solutions in

Fig.3 Intrinsic Viscosity - Time Profiles for PET Solutions 50% Phenol: 50% 1,2-Dichlorobenzene Solvent Mixture

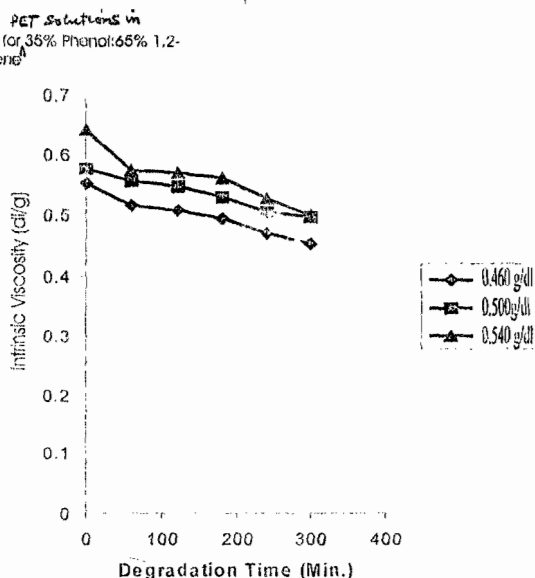
Fig.4 Intrinsic Viscosity - Time Profiles for PET Solutions 65% Phenol:35% 1,2-Dichlorobenzene Solvent Mixture

0.500 g/dl, while at 0.540 g/dl, the profile was irregular. Slopes were determined to be 3.06×10^{-4} and 2.63×10^{-4} dlg^{-1}min^{-1} for 0.460 and 0.500 g/dl concentrations respectively. This shows a decrease in degradation rate with increase in polymer concentration. This contrasts with earlier observations. It obviously shows a considerable effect of solvent composition on degradation rate With 65% phenol, the solvent exhibits high thermodynamic capacity, such that the polymer chains are extensively extended (i.e. under tension). This tension factor increases degradation rate.

The result is that at higher polymer concentration, the degradation rate will be so high, (i.e. many macro radicals will be formed at the early stages of degradation process). Since many radicals are formed, there is also a possibility of recombination of the macro radicals leading to the formation of both linear and cross-link systems. The recombination could occur simultaneously with degradation, leading to an increase as well as a decrease in molecular weight occurring at

the same time. The decrease in solution viscosity will therefore depend on the extent to which degradation reactions outweigh recombination reactions.

From the results obtained, it can be inferred that recombination reactions occurred the least at the lowest concentration of 0.460 g/dl since the lowest amount of initial macro radicals were present. This explains why the slope at 0.460g/dl poly (ethylene terephthalate) concentration was the highest. Generally, the macro radical recombination reaction effect seems to increase with polymer concentration. At a concentration of 0.540 g/dl, there seemed to be a period of predominant degradation (0-60 minutes), a period of predominant recombination reactions (60-180 min) and a period associated with both degradation and recombination reactions (180-300 min)

CONCLUSION

Poly (ethylene terephthalate) has been found to degrade in solution at a much lower temperature of

145°C than the bulk undissolved polymer which is reported to be stable up to a temperature 295 °C and degrades within a temperature range of 300-550 °C . At low phenol concentration of the solvent mixture, the rate of poly (ethylene terephthalate) degradation increases with increase in polymer concentration. At 65% phenol concentration, the rate of degradation decreases with increase in polymer concentration.

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