

EFFECT OF COPPER (II) PHTHALOCYANINE CONCENTRATION ON POLY (ETHYLENE TEREPHTHALATE) DEGRADATION IN PHENOL: 1,2-DICHLOROBENZENE SOLVENT MIXTURE.

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ABSTRACT

Poly (ethylene terephthalate) was dissolved in Phenol: 1,2-dichloro benzene solvent mixtures of 35 %: 65 %, 50 %: 50 %, 65 %: 35 % by weight and degraded at 143 ± 2 °C. The effect of pigment (copper (II) phthalocyanine) concentration on poly (ethylene terephthalate) degradation in solution was investigated by dilute solution viscometry, using 0.004g/dl, 0.008 g/dl and 0.012 g/dl pigment concentrations respectively in 0.5g/dl poly (ethylene terephthalate) concentration.

It was found that the rate of poly (ethylene terephthalate) degradation increased with increase in copper (II) phthalocyanine concentration from 0.004g/dl to 0.008g/dl and decreased when the concentration was increased from 0.008g/dl to 0.012g/dl.

KEY WORDS; Poly (ethylene terephthalate), Copper (II) phthalocyanine (Pigment Blue), Degradation.

INTRODUCTION

Poly (ethylene terephthalate), abbreviated as PET (Fig. 1) is formed by the condensation of terephthalic acid or its dimethyl ester with glycol. It is used in the manufacture of textile fibres, tyre cords, photographic films, magnetic tapes, typewriter ribbons and other structural objects. The manufacturing process involves heating the polymer to high temperatures, which results in partial degradation of the polymer. In highly sensitive process, such as the melt spinning of poly (ethylene terephthalate) for the production of polyester fibres, the extent of partial degradation affects the quality of the fibres and the overall quality of the resultant fabric (Bresler, 1960). Such production processes are monitored by viscometric analysis of the intermediate products formed (Staudinger and Heuer, 1930).

Bulk undissolved poly (ethylene terephthalate) is known to degrade within the temperature range of 300–500 °C (Allcock and Lampe, 1981). The products obtained from the degradation process are mainly oxygen containing compounds, such as carbon dioxide, acetaldehyde and terephthalic acid (Masuda et al, 1996). In modern poly (ethylene terephthalate) spinning plants, coloured polyester fabrics are produced directly from the spinning process by mass pigmentation methods. This involves dispersing a pigment in the molten polymer as the polymer is being melted in the extruder. The pigment is being entrapped in the fibre as it is being formed at the spinneret.

Structural and chemorheological modification of poly (ethylene terephthalate) in the melt phase with

low molecular weight multifunctional glycidyl compounds as reactive additives have been investigated (Dhavalikar, 2003). A number of investigations on the degradation of poly (ethylene terephthalate) have been reported (Goto et al, 2000; Song et al, 2002; Szczepanowska and Wilson, 2000; Gubanski and Montanari, 1992). However, literature on poly (ethylene terephthalate) degradation in solution is still scanty.

The effects of some cobalt (II) compounds on the degradation of some polymers in solution have been reported (Betts and Uri, 1966). Copper (II) derivative of phthalocyanine (Fig. 2) is one of the pigments used in colouring poly (ethylene terephthalate) fibres. Properties of this pigment have been reported (Dent and Linstead, 1934), but its effect on poly (ethylene terephthalate) degradation in solution has not been reported. This paper reports the effect of copper (II) phthalocyanine (pigment blue) on poly (ethylene terephthalate) degradation in solution.

EXPERIMENTAL

MATERIALS

Poly (ethylene terephthalate) chips (Lucky Polymers), were obtained from Horizon Fibres, Port Harcourt. They were transparent and colourless plastic 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

Table 1: Efflux Time Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 35 % Phenol: 65 % 1,2-dichlorobenzene Solvent Mixture at 25°C.

Conc. of Pigment blue (g/dl)	Conc. of PET (g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min.)					
			0	60	120	180	240	300
0.004	0.500	70.20	97.30	95.50	94.87	94.66	93.50	93.29
0.008	0.500	70.20	97.41	95.29	94.70	94.30	93.38	93.09
0.012	0.500	70.20	97.35	97.22	95.45	95.23	94.29	93.77

Table 2: Efflux Time Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 50 % Phenol: 50 % 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of Pigment blue (g/dl)	Conc. of PET (g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min.)					
			0	60	120	180	240	300
0.004	0.500	93.013	128.873	126.435	125.480	125.300	123.735	123.300
0.008	0.500	93.013	128.950	126.000	125.315	124.685	123.390	123.020
0.012	0.500	93.013	129.000	128.725	126.335	125.850	124.525	124.000

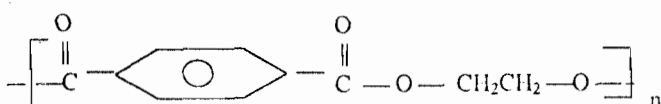


Fig. 1: Poly (ethylene terephthalate)

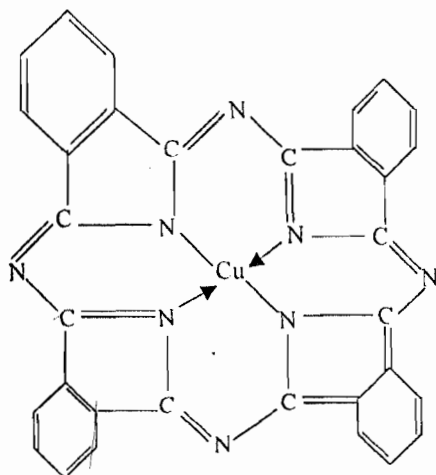


Fig. 2: Copper (II) Phthalocyanine (Pigment Blue)

and was of analytical reagent (b.p. 178 – 180°C). All other chemicals used were of laboratory reagent.

METHOD

Preparation of Solvent Mixture

Phenol crystals (1000g) 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 of the solvent mixture. 35 %: 65 % and 65 %: 35 % by weight Phenol: 1,2-dichlorobenzene solvent mixtures were next prepared.

Preparation of Poly (ethylene terephthalate) Solution

1.25g of the poly (ethylene terephthalate) chips were introduced into a 100 ml volumetric flask and the prepared solvent mixture (50 ml) was next added. This mixture was heated (143±2 °C) over a silicon oil bath using a thermostatically-controlled electric heater. The flask and its contents were shaken at 150 rpm to obtain homogeneous solution.

Determination of Melting Temperature, Ash Content and Acid Number of Poly (ethylene terephthalate)

These parameters were determined according to an earlier reported procedure (Otaigbe et al, 2003).

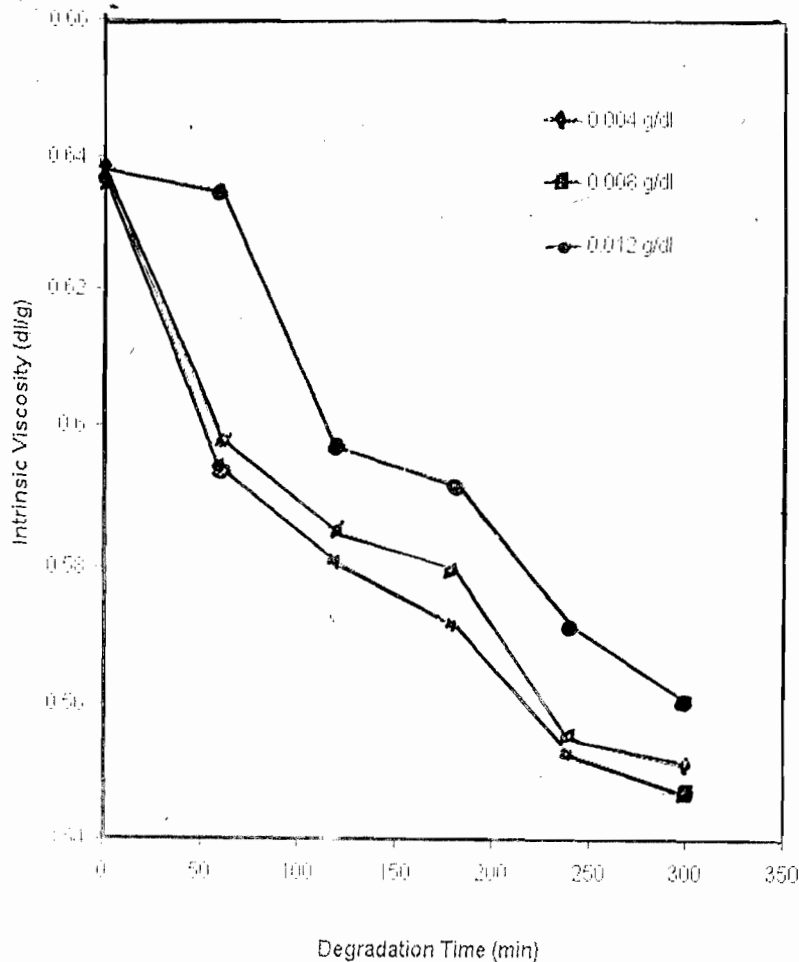


Fig. 3: Intrinsic Viscosity -Time Profiles for PET Solutions in 35% Phenol: 65% 1,2-Dichlorobenzene Solvent Mixture.

Table 3: Efflux Time Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 65 % Phenol: 35 % 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of Pigment blue (g/dl)	Conc. of PET (g/dl)	Solvent Efflux Time (Sec)	Efflux Time Values at Various Degradation Time (min)					
			0	60	120	180	240	300
0.004	0.500	128.560	177.830	174.600	173.310	173.050	170.840	170.030
0.008	0.500	128.560	178.100	174.000	173.050	172.150	170.400	169.000
0.012	0.500	128.560	178.210	174.750	174.450	173.800	172.100	171.150

Viscosity Measurements

Viscosity measurements were carried out according to standard procedure (DIN, 1985) using a mixture of phenol and 1,2-dichlorobenzene solvent and at a temperature of 25°C. 35%: 65%, 50%: 50% and 65%: 35% by weight phenol: 1,2-dichlorobenzene solvent mixtures were prepared according to the procedure outlined in section 2.2.1. 1.25g poly (ethylene terephthalate) chips were dissolved in 50 ml of each of the solvent mixtures and

10 mg copper (II) phthalocyanine (pigment blue) was added. The mixture, contained in a 100 ml volumetric flask was allowed to agitate in an oil bath (143±2 °C) at a constant rate of 150 rpm.

At intervals of one hour, 10 ml of the solution was withdrawn with a pipette, introduced into a 50 ml volumetric flask and then made up to the 50 ml mark with the pure solvent. The resultant solution was used for viscosity measurements. The efflux time of the

Table 4: Intrinsic Viscosity Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 35 % Phenol: 65 % 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of Pigment blue (g/dl)	Conc. of PET (g/dl)	Intrinsic Viscosity Values (dl/g) at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.004	0.500	0.637	0.598	0.585	0.580	0.555	0.551
0.008	0.500	0.639	0.594	0.581	0.572	0.553	0.547
0.012	0.500	0.638	0.635	0.597	0.592	0.572	0.561

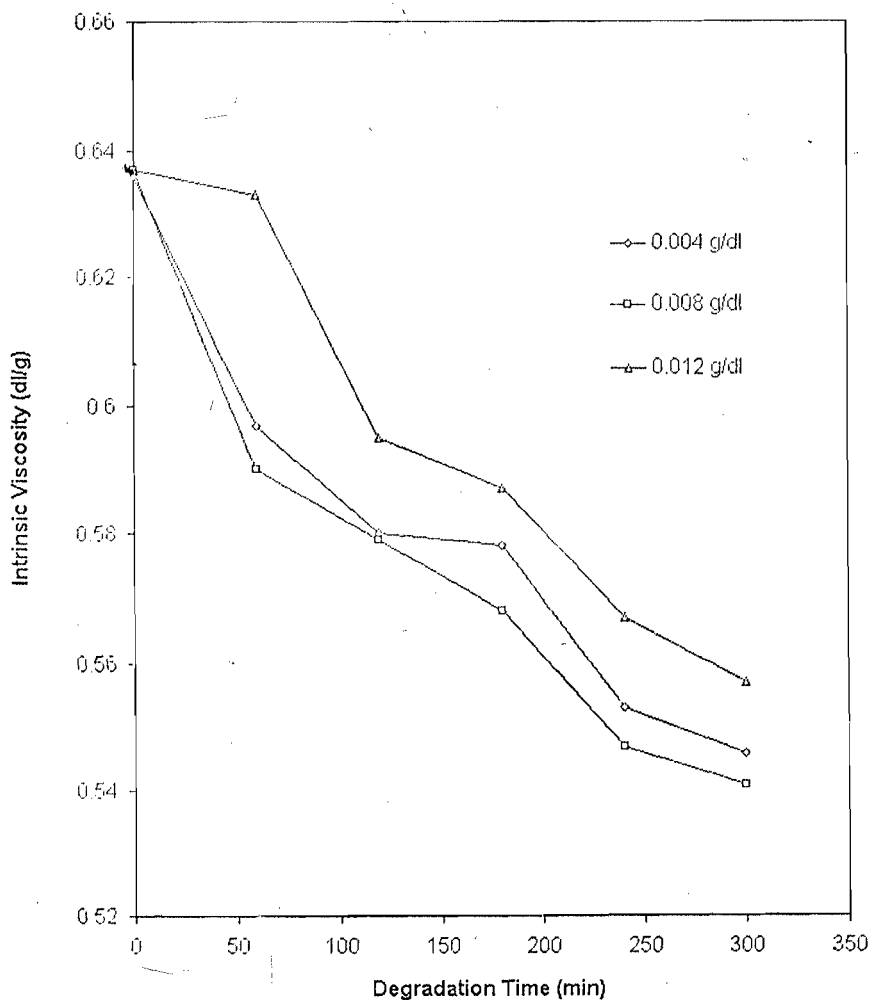


Fig. 4: Intrinsic Viscosity -Time Profiles for PET Solutions in 50% Phenol: 50% 1,2-Dichlorobenzene Solvent Mixture.

solution, t and that of the solvent, t_0 , were measured using a "Hanhart" electronic stopwatch. The experiment was repeated using 20 mg and 30 mg of the pigment blue respectively. Results are shown in tables 1–3. Relative viscosity (η_{rel}) values were calculated using the equation.

$$\eta_{rel} = \frac{t}{t_0} \dots\dots\dots (1) \dots\dots\dots (1)$$

Intrinsic viscosity $[\eta]$ values were determined from a graph which relates relative viscosity for poly (ethylene

terephthalate) dilute solutions in phenol / 1,2-dichlorobenzene solvent mixtures (DIN, 1985). Results of intrinsic viscosities at various degradation times are shown in tables 4–6.

RESULTS AND DISCUSSION

Characterisation of Poly (ethylene terephthalate)

The results obtained for the ash content, melting temperature and Acid number for poly (ethylene terephthalate) are in conformity with the earlier reported values (Otaigbe et al, 2003).

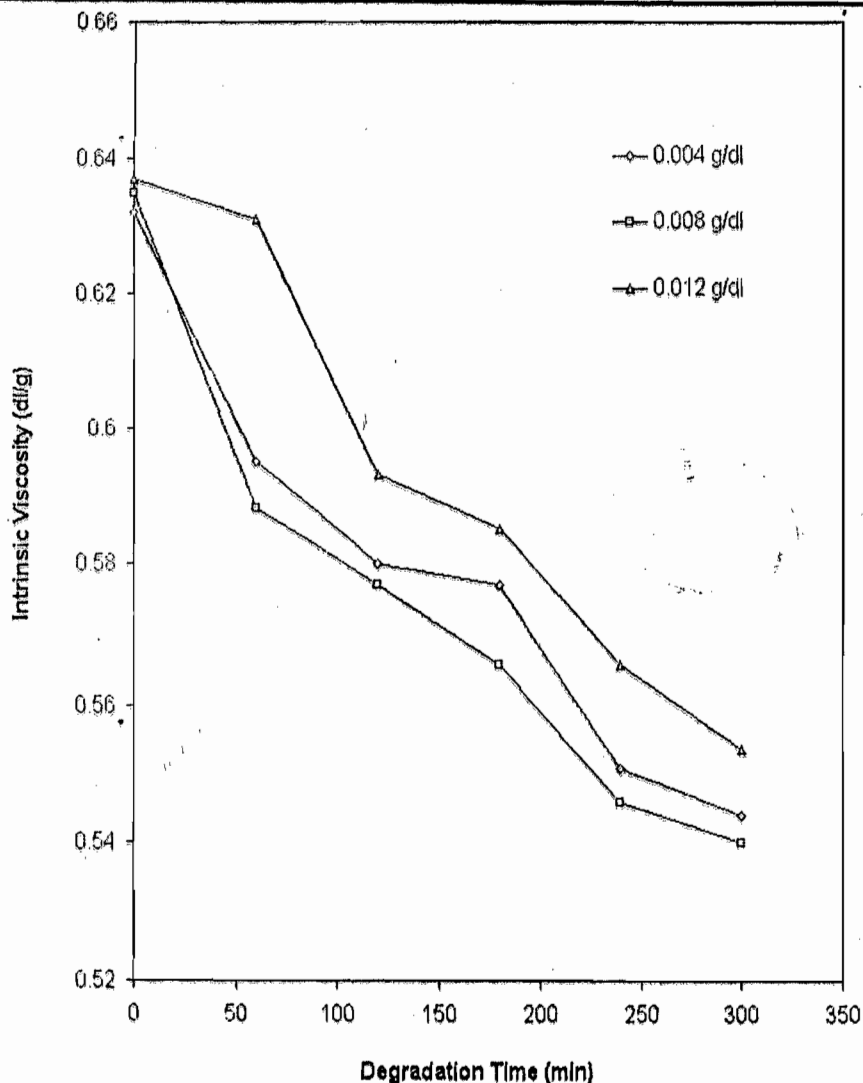


Fig. 5: Intrinsic Viscosity -Time Profiles for PET Solutions in 65% Phenol: 35% 1,2-Dichlorobenzene Solvent Mixture.

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 were 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 - 70.20 seconds, while 50% phenol gave a value in the range, 91.91-95.84 seconds. The 65% phenol: 35% 1,2-dichlorobenzene mixture gave an afflux time ranging from 128.56 - 129.70 seconds. These variations in efflux time of the solvent mixtures can be accounted for on the basis that 1,2-dichlorobenzene in 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 the resulting mixture will be higher than that of 1,2-dichlorobenzene. Similarly, as the concentration of phenol in the blended solvent increases, the viscosity increases.

Effect of Copper (II) Phthalocyanine 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, which also indicate the effects of pigment (copper phthalocyanine) concentration on the rate of degradation are shown in figs 3, 4, and 5, for solvent mixture composition of 35%: 65%, 50%: 50%, and 65%: 35% by weight phenol: 1,2-dichlorobenzene respectively. These plots show that the lowest viscosity (highest degradation) was recorded at the pigment concentration of 0.008g/dl, while the least degradation occurred at the pigment concentration of 0.012g/dl.

This observation is common to all the solvent compositions used.

This result shows that the rate of degradation increases as the concentration of the pigment is increased from 0.004 g/dl to 0.008 g/dl and decreased when the concentration of pigment increased from 0.008g/dl to 0.012 g/dl. The increase in degradation rate with increase in pigment blue concentration may be attributed to the catalytic activity of copper (II) on the degradation process.

The observed decrease in the degradation rate when the pigment concentration was increased from 0.008g/dl to 0.012 g/dl could be as a result of

Table 5: Intrinsic Viscosity Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 50 % Phenol: 50 % 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. of Pigment blue (g/dl)	Conc. PET (g/dl)	Intrinsic Viscosity Values (dl/g) at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.004	0.500	0.636	0.597	0.580	0.578	0.553	0.546
0.008	0.500	0.637	0.590	0.579	0.568	0.547	0.541
0.012	0.500	0.637	0.633	0.595	0.587	0.567	0.557

Table 6: Intrinsic Viscosity Values for Poly (ethylene terephthalate) and Copper (II) phthalocyanine (Pigment blue) Solutions in 65 % Phenol: 35 % 1,2-dichlorobenzene Solvent Mixture at 25°C

Conc. Of Pigment blue (g/dl)	Conc. of PET (g/dl)	Intrinsic Viscosity Values (dl/g) at Various Degradation Time (min.)					
		0	60	120	180	240	300
0.004	0.500	0.632	0.595	0.580	0.577	0.551	0.544
0.008	0.500	0.635	0.588	0.577	0.566	0.546	0.540
0.012	0.500	0.637	0.631	0.593	0.585	0.566	0.554

molecular weight increase due to recombination reactions of the already formed macro-radicals. The catalytic activity may have been so high at 0.012g/dl pigment concentration that there was a very high initial rate of formation of macro-radicals, which had to recombine in the later stages thereby inhibiting degradation. This is comparable to the observation reported by Betts and Uri that some cobalt compounds which are degradation catalysts at low concentrations become inhibitors at high concentrations (Betts and Uri, 1966)

CONCLUSION

This study has shown that Poly (ethylene terephthalate) is susceptible to thermal degradation when dissolved at relatively low temperature of about 145°C in contrast with bulk undissolved Poly (ethylene terephthalate) said to be stable up to the temperature of 295°C. At 0.5g/dl Poly (ethylene terephthalate) concentration used in the study, the rate of degradation increased as the Copper (II) phthalocyanine (pigment blue) concentration was increased from 0.004 g/dl to 0.008 g/dl but decreased when the pigment concentration was increased from 0.008 g/dl to 0.012 g/dl. This shows Copper (II) phthalocyanine at low concentration catalyses degradation of poly (ethylene terephthalate) but acts as inhibitor at high concentrations.

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