EFFECT OF RATE OF AGITATION ON POLY (ETHYLENE TEREPHTHALATE) DEGRADATION IN PHENOL. 1,2-DICHLOROBENEZENE SOLVENT MIXTURE

J. O. E. OTAIGBE, H. C. NWOKONKWO and C. C. ONYEMENONU, Snr.

ABSTRACT

The evaluation of the acid number, ash content and melting temperature of poly (ethylene terephthalate) has been reported (Otaigbe et al, 2003). The polymer was dissolved in phenol: 1,2 dichlorobenzene solvent mixture of 35%: 65% and 50%: 50% by weight and then degraded at 143±2°C. The effect of the rate of agitation on poly (ethylene terephthalate) degradation in solution was investigated by dilute solution viscometric measurements on 0.5 g/dl polymer concentration and agitation rates of 150 revolutions per minute (rpm), 180 rpm and 190 rpm respectively.

Results show that the rate of degradation increases generally with increase in the rate of agitation as evidenced by the reduction in intrinsic viscosities under similar conditions. Intrinsic viscosities were found to be 0.621, 0.609 and 0.604 at 150 rpm, 180 rpm and 190 rpm respectively for 35%: 65% phenol: 1,2-dichlorobenzene solvent composition at degradation time of 60 minutes. At degradation time of 300 minutes, intrinsic viscosities were found to be 0.548, 0.547 and 0.544 at 150 rpm, 180 rpm and 190 rpm respectively for the same solvent composition.

For 50%: 50% by weight phenol: 1,2-dichlorobenzene solvent composition, intrinsic viscosities were found to be 0.601, 0.596 and 0.593 at a degradation time of 60 minutes and agitation rates of 150 rpm, 180 rpm and 190 rpm respectively. Similar trend was observed for 300 minutes degradation time, where intrinsic viscosities of 0.562, 0.555 and 0.551 were recorded at 150 rpm, 180 rpm and 190 rpm respectively.

KEY WORDS: Poly (ethylene terephthalate), Degradation, Agitation.

INTRODUCTION

Poly (ethylene terephthalate), (Fig. 1) is a linear polymer formed by the condensation polymerisation of terephthalic acid or its dimethyl ester with glycol. It has application in the manufacture of structural materials, such as, textile fibres, photographic films, gear wheels, magnetic tapes, etc. Its properties and performance have been reported (Fuller, 1940; Bunn, 1953). Degradation involves the deterioration of those properties of polymers which make them useful commercially (Reiner, 1966). Bulk undissolved poly (ethylene terephthalate), (PET) is known to degrade within the temperature range of 300-550°C (Allcock and Lampe, 1981), yielding mainly oxygen-containing compounds, such as carbon dioxide, acetaldehyde and terephthalic acid as products. (Masuda et al, 1996).

Mechanical degradation of polymers result when polymers are subjected to mechanical forces. In polymer solutions, degradation of this nature has been found to occur as a result of shaking, beating, high speed stirring, turbulent flow or droplet formation (Grassie, 1956). Degradation of this nature is usually measured by decrease in the solution viscosity. Similar breakdown of molecular structure occurs during milling and cutting in solid polymers. A typical example is the mastication of natural rubber.

It has been shown that high speed stirring of polystyrene and poly (isobutylene) in various solvents is most effective in causing mechanical degradation (Cameron, 1962). It has also been reported that mechanical degradation result from chain entanglement, which play major part in chain scission (Davies,1962). It was concluded from series of experiment that oxidation of polymer macro- radicals is the main cause of decrease in molecular weight as the macro- radicals would recombine in the absence of oxygen (Watson and Pyke, 1958). Endurance of poly (ethylene terephthalate) subjected to electrical and thermal stresses simultaneously applied (multi-stress) has been reported (Gubanski and Montanari, 1992).

Studies on poly (ethylene terephthalate) degradation has been reported (Goto et al, 2000; Szczepanowska and Wilson, 2000; Song et al, 2000; Dhavalikar, 2003). This paper reports the effect of agitation rate 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 crystal was a product of May and Baker. 1,2-dichlorobenzene was obtained from Riedel de Haen

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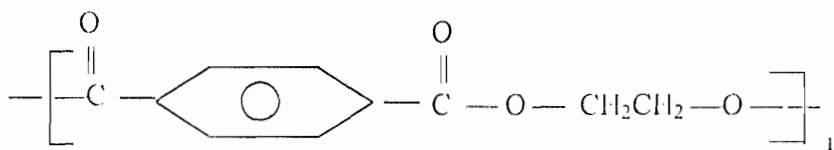
Fig. 1: Poly (ethylene terephthalate)

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

Rate of Agitation (rpm)	Conc. of PET (g/dl)	Solvent Efflux Time (sec)	Efflux Time Values for Various Degradation Time (min.)					
			0	60	120	180	240	300
150	0.500	70.01	97.25	96.33	95.21	94.92	93.63	92.93
180	0.500	70.20	97.52	96.03	95.00	94.90	93.71	93.09
190	0.500	70.20	97.52	95.78	94.80	94.23	93.51	92.98

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

Rate of Agitation (rpm)	Conc. of PET (g/dl)	Solvent Efflux Time (sec)	Efflux Time Values for Various Degradation Time (min.)					
			0	60	120	180	240	300
150	0.500	92.13	128.03	125.54	124.84	124.29	123.78	123.14
180	0.500	91.26	126.78	124.00	123.50	122.90	122.00	121.51
190	0.500	91.26	126.78	123.85	123.41	122.76	121.83	121.30

00and was of analytical reagent (b.p.178–180°C). All other chemicals used were of laboratory reagent.

METHOD

Preparation of Solvent Mixture

1000g phenol crystals were placed in a "memert" oven for five 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 to give 50%: 50% by weight phenol: 1,2-dichlorobenzene solvent mixture. The bottle was corked and the warm mixture was shaken using an electronic shaker at the rate of 160–172 revolution per minute (rpm) for 1.5 hours. The solvent mixture was finally allowed to cool to room temperature. 35%: 65% by weight phenol: 1,2-dichlorobenzene solvent mixture was also prepared.

Preparation of Poly (ethylene terephthalate) Solution

A pre-determined weight (1.25 g) of the poly (ethylene terephthalate) chips were introduced into a 100 ml volumetric flask and 50 ml of the prepared solvent mixture was next added. This mixture was heated (143±2 °C) over a silicone oil bath using a thermostatically controlled electric heater. The flask and its content were shaken at 150 rpm until complete dissolution occurred.

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).

Viscosity Measurements

Viscosity measurements were carried out according to standard procedure (DIN, 1985) using phenol/1,2-dichlorobenzene mixture as a solvent and at a temperature of 25°C. 1.25 g poly (ethylene terephthalate) was dissolved in 50 ml 35%: 65% and 50%: 50% by weight phenol: 1,2-dichlorobenzene solvent mixtures respectively in 100 ml volumetric flask. The solution was allowed to agitate at a constant rate of 150 rpm in a hot oil bath (143 ± 2 °C). At intervals of 60 minutes, 10 ml of the solution (solution A) was pipetted into a 50 ml volumetric flask and then made up to the mark using the pure solvent (solution B). The viscosity of each solution B prepared at intervals was measured. The experiment was repeated using agitation rate of 180 rpm and 190 rpm respectively. Concentration of poly (ethylene terephthalate) in solution B was calculated using the following equation:

$$X = \frac{10 x A}{50} \quad \text{...(1)}$$

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Table 3: Intrinsic Viscosity Values for Poly (ethylene terephthalate) Solutions in 35% phenol: 65% 1,2-dichlorobenzene Solvent Mixture at 25°C

Rate of Agitation (rpm)	Conc. of PET (g/dl)	Intrinsic Viscosity Values (dl/g) for Various Degradation Time (min.)					
		0	60	120	180	240	300
150	0.500	0.641	0.621	0.597	0.591	0.564	0.548
180	0.500	0.641	0.609	0.587	0.585	0.560	0.547
190	0.500	0.641	0.604	0.583	0.571	0.556	0.544

Table 4: Intrinsic Viscosity Values for Poly (ethylene terephthalate) Solutions in 50% phenol: 50% 1,2-dichlorobenzene Solvent Mixture at 25°C

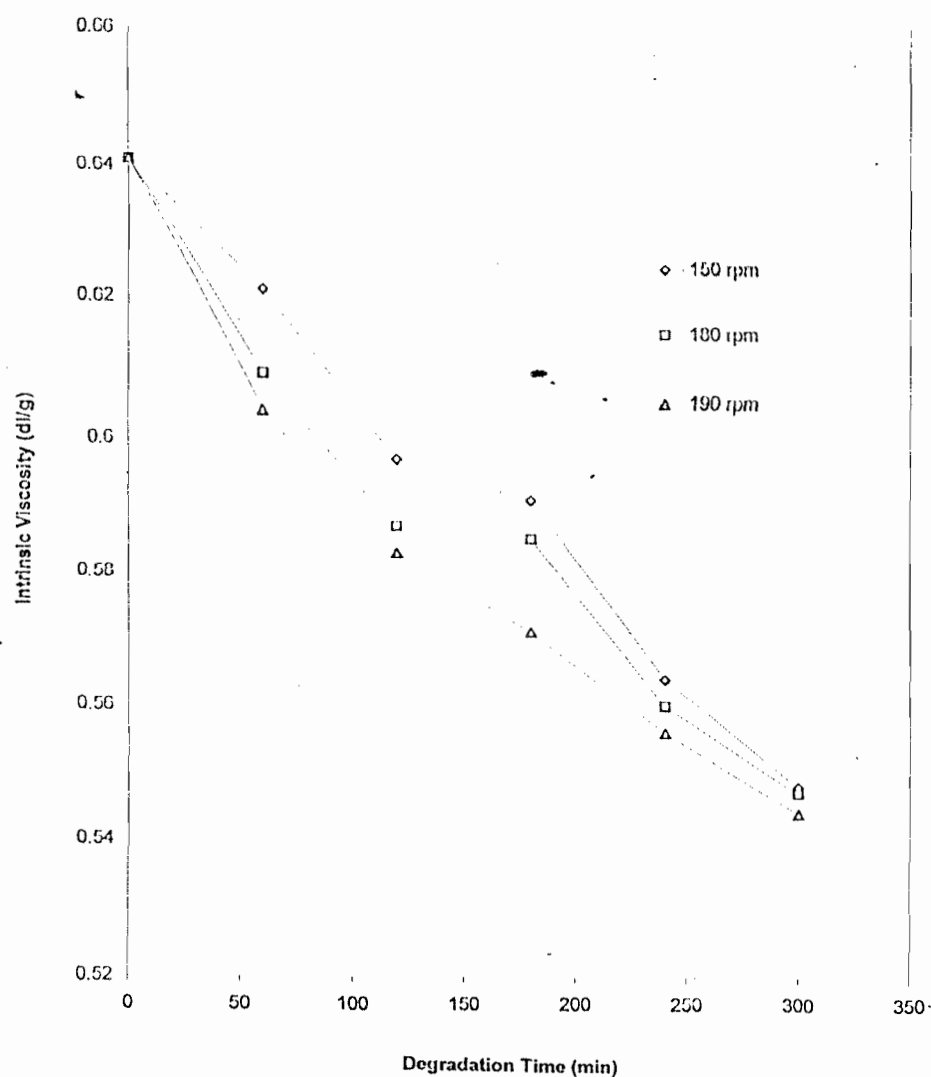| Rate of Agitation (rpm)	Conc. of PET (g/dl)	Intrinsic Viscosity Values (dl/g) for Various Degradation Time (min.)					
		0	60	120	180	240	300
150	0.500	0.641	0.601	0.590	0.581	0.573	0.562
180	0.500	0.641	0.596	0.587	0.578	0.563	0.555
190	0.500	0.641	0.593	0.586	0.575	0.560	0.551

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

where, x = concentration of Solution B (g/50ml)

A = weight of PET used in preparing Solution A (g).

Relative Viscosities (η_{rel}) were calculated using the equation,

$$\eta_{rel} = \frac{t}{t_0} \qquad \text{...................................... (2)}$$

where, t = efflux time of solution

t_0 = efflux time of solvent.

Efflux time results are shown in tables 1-2. The calculated relative viscosities were used in determining intrinsic viscosities, [η] result shown in tables 3 – 4, from graph relating relative viscosities with intrinsic viscosities for poly (ethylene terephthalate) dilute solution in phenol / 1,2-dichlorobenzene solvent mixture (DIN, 1985).

RESULTS AND DISCUSSION

Characterisation of Poly (ethylene terephthalate)

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

Viscosity of Solvent Mixtures

Phenol: 1,2-dichlorobenzene mixtures of 35%: 65% and 50%: 50% 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, 91.19 – 95.84 seconds.

These variations in efflux times 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 the
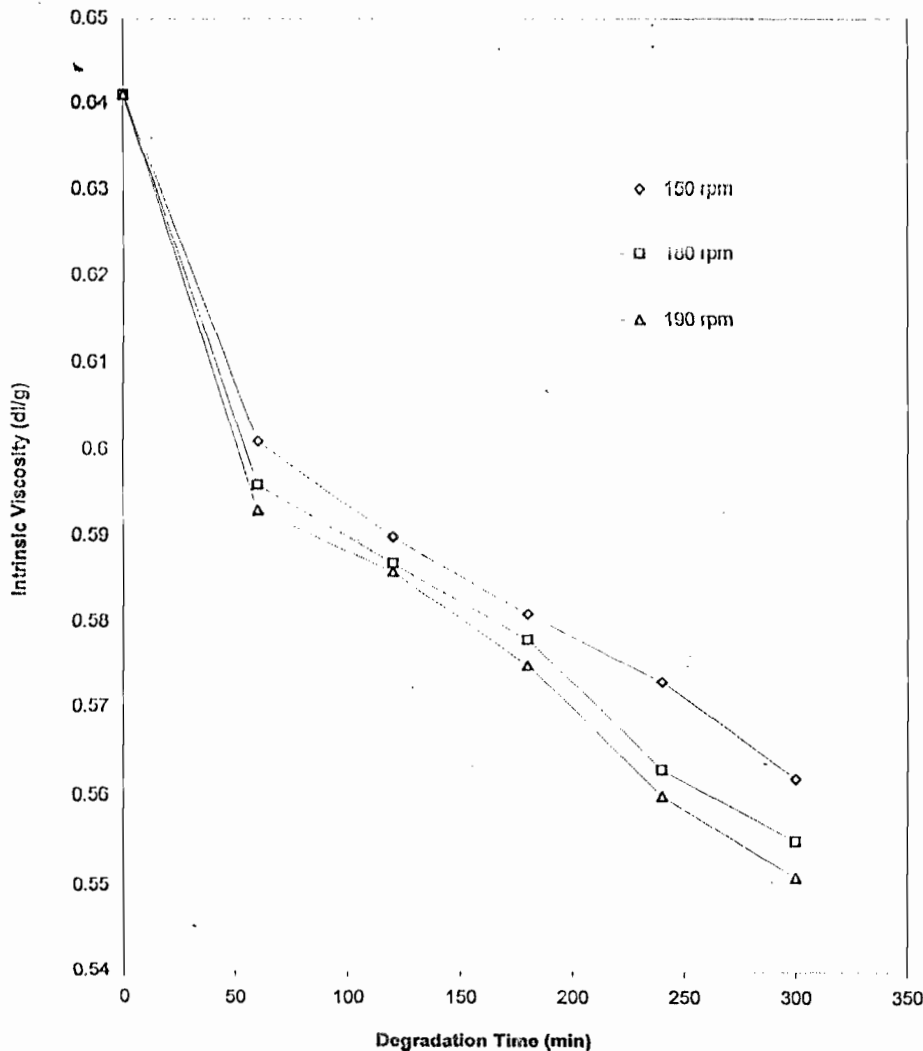

Fig. 3:   Intrinsic Viscosity -Time Profiles for 50% Phenol: 50% 1,2-Dichlorobenzene Solvent Mixture.

resulting mixture will be higher than that of 1,2-dichlorobenzene. Similarly, as the composition of phenol in the mixture increases, the viscosity of the solvent mixture increases accordingly.

Effect of Rate of Agitation on Poly (ethylene terephthalate) Degradation.

The effect of the rate of agitation on the degradation of poly (ethylene terephthalate) solution in phenol/1,2-dichlorobenzene solvent mixture was studied by dilute solution viscometry using 35%: 65% and 50%: 50% by weight phenol: 1,2-dichlorobenzene. The efflux time and intrinsic viscosity results are shown in tables 1–2 and 3–4 respectively for agitation rates of 150 rpm, 180 rpm and 190 rpm.

Plots of intrinsic viscosity versus degradation time which indicate the effect of agitation rate on the rate of degradation are shown in Fig. 2 and 3 for 35%: 65% and 50%: 50% by weight phenol: 1,2-dichlorobenzene solvent mixtures respectively. The plots show a general increase in degradation rate with increase in agitation rate under the same conditions. For instance, at degradation time of 60 minutes (35%: 65% phenol: 1,2-dichlorobenzene solvent mixture), intrinsic viscosity values were determined as 0.621, 0.609 and 0.604 at 150 rpm, 180 rpm and 190 rpm agitation rates respectively; and 0.548, 0.547 and 0.544 respectively at a degradation time of 300 minutes for the same solvent composition. For 50%: 50% phenol: 1,2-dichlorobenzene solvent composition, intrinsic viscosity values at 150 rpm, 180 rpm and 190 rpm (at 60 minutes degradation time) were 0.601, 0.596 and 0.593 respectively; and 0.562, 0.555 0.551 respectively at a degradation time of 300 minutes. Degradation results in reduction in intrinsic viscosities. This effect is as a result of increased tension on the polymer chains in solution due to increased agitation rate. The result is that the polymer chains will rupture mechanically, thereby increasing the rate of degradation.

CONCLUSION

The poly (ethylene terephthalate) degrades in solution at a much lower temperature of 145°C than pure poly (ethylene terephthalate) known to be stable up to a temperature of 295°C and degrades within a temperature range of 300–550°C. This result has further demonstrated that the rate of degradation increases with increase in the rate of agitation of poly (ethylene terephthalate) in solution under similar conditions.

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