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Kinetic Study of Grafting Acrylamide onto Poly(ethylene terephthalate) Fibres

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Graft copolymerization of acrylamide onto poly(ethylene terephthalate) fibres was carried out in benzyl alcohol medium using hydrogen peroxide as an initiator. Per cent graft yield and rate of grafting were determined. The rate of grafting was found to be proportional to 0.64 and 1.11 powers of initiator and monomer concentrations, respectively. The energy of activation value was calculated as 34.3 kJ/mol by carrying out the graft copolymerization reaction at three different temperatures ranging from 70 to 95°C. The overall rate constants were also determined.

Key Words: Rate of grafting; Acrylamide; Hydrogen peroxide; Poly(ethylene terephthalate) fibre.

INTRODUCTION

Graft copolymerization is a well-known important method for modification of the chemical and physical properties of natural[1–4] and synthetic polymers.[5–13] Poly(ethylene terephthalate) (PET), in fibre form, is one of the polymers that was attempted to be modified by graft copolymerization. Many vinyl monomers such as acrylic acid[14], methyl methacrylate[15], and methacrylic acid[16] were used for grafting onto PET fibres. Many of the studies carried out on this subject are directed to investigate the properties of grafted fibres and to determine the factors affecting the grafting reaction. But there are some studies to obtain some kinetic data about these reactions as well. For example, in the grafting of acrylic acid onto PET fibres using benzoyl peroxide, Saçak and Oflaz have reported that the grafting rate is proportional to the 0.92 and 2.33 powers of the initiator and monomer concentrations, respectively.[14] In the grafting of methacrylic acid with azobisizobutyronitrile[17], the above orders become 0.94 and 1.22. It has also been stated that grafting rate is of 0.95 order with respect to initiator concentration in the grafting of methacrylic acid.[18]

Activation energies of various grafting systems are also given in the literature. The activation energies of grafting of methyl methacrylate[19] and methacrylic acid[17] onto PET fibres were reported to be 66.9 kJ/mol and 130.4 kJ/mol, respectively.

In this article we report the relation between the rate of grafting and the acrylamide and hydrogen peroxide concentrations and some kinetic parameters related to the grafting reaction have been determined.

EXPERIMENTAL

The multifilament PET fibres (30 filament, 110 dTex) obtained from SASA Co (Adana, Turkey) were Soxhlet-extracted with acetone for 8 h and dried at room temperature before use. Acrylamide (AAM) (BDH) was recrystallized from acetone. Hydrogen peroxide (H_2O_2) (Merck) and benzyl alcohol (Merck) were of chemically pure grade.

Grafting Procedure: The fibre sample (W_i g) was placed into the polymerization tube containing required amount of monomer and initiator. The total volume was made up to 20 mL using benzyl alcohol. The mixture was purged with nitrogen for 20 min and the polymerization tube was placed into a water bath (Lauda D 40S, Germany) where temperature could be controlled to within ± 0.1°C. The nitrogen purging was continued throughout the grafting reaction, which also facilitated the mixing of the polymerization system. The fibre sample taken from the polymerization medium at the end of the predetermined polymerization period was washed with boiling water several times, then Soxhlet-extracted with water for an additional 8 h. Finally, the fibre sample was dried and weighed, and per cent graft yield (G%) was gravimetrically determined from the weights of grafted and original fibres.

Rate Measurement: The rate of grafting (Rg) was calculated as follows; Rate of grafting $(Rg) = (G\% \cdot W_i \cdot 1000)/(100 \cdot V \cdot t \cdot M)$ where G% is per cent graft yield, W is weight of original fibre, V is total volume of the reaction mixture, t is reaction time, and M is molecular weight of AAM.

RESULTS AND DISCUSSION

Preliminary studies indicate that no grafting was observed under 4 h. Therefore, all successive experiments have been carried out for polymerization time 4 h. The number of studies concerning the grafting of vinyl monomers onto PET fibres using H_2O_2 is quite limited. The grafting of acrylamide onto PET fibres using this initiator was recently reported by us.[11]

In a study where a monomer is grafted onto PET fibres inevitably homopolymer of the monomer is obtained together with the grafted fibres. Therefore the monomer in the medium is used in both the grafting and homopolymer formation processes. In such a system, the relation between the rate of grafting and the monomer and initiator concentrations can be written as:[14, 15]

$$Rg = k\,[\text{initiator}]^m[\text{monomer}]^n$$

Here m and n can be experimentally determined by using the logarithmic form of the equation given above:

$$\log Rg = \log k + \log [\text{initiator}]^m + \log [\text{monomer}]^n$$

Effect of H_2O_2 concentration on Rg: The concentration of H_2O_2 was varied from 0.046 to 0.160 mol/L while keeping other experimental conditions as constant (Table-1). The Rg values increased with an increase in $[H_2O_2]$.

TABLE-1
DEPENDENCE OF RATE OF GRAFTING (Rg) ON HYDROGEN PEROXIDE CONCENTRATION

$[H_2O_2]$ (mol/L)	G (%)	$Rg \times 10^6$ (mol/L s)	log $[H_2O_2]$ + 2	log Rg + 7
0.046	3.33	0.228	0.658	0.358
0.091	4.50	0.308	0.959	0.488
0.118	6.00	0.410	1.073	0.613
0.160	7.50	0.513	1.204	0.710

[AAM] = 1.830 mol/L; time = 4 h; temp = 95°C

The direct plot Rg *vs.* log $[H_2O_2]$ (Fig. 1) was found to be a straight line with a slope of 0.64. This indicates that the rate of grafting was proportional to the 0.64 power of the hydrogen peroxide concentration.

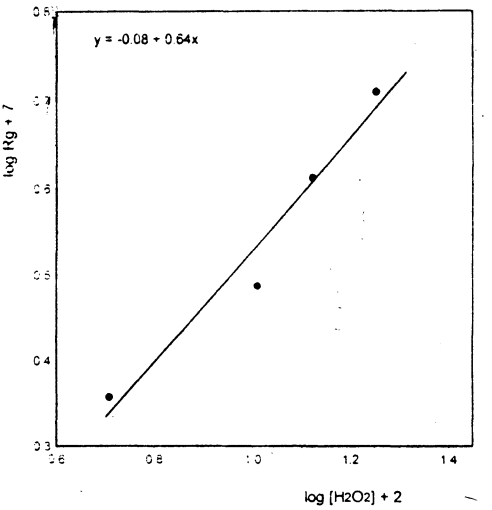

Fig. 1. Rates of grafting reactions *vs.* initiator concentration

Effect of AAM concentration on Rg: As represented in Table-2, experimental results were obtained by changing the concentration of acrylamide in the range from 0.455 to 1.830 mol/L while keeping other experimental conditions as constant.

TABLE-2
DEPENDENCE OF RATE OF GRAFTING (Rg) ON ACRYLAMIDE CONCENTRATION

[AAM] (mol/L)	G (%)	$Rg \times 10^6$ (mol/L s)	log [AAM] + 1	log Rg + 7
0.455	1.67	0.114	0.658	0.057
0.909	3.67	0.251	0.959	0.399
1.273	5.33	0.365	1.105	0.562
1.455	6.42	0.439	1.163	0.642
1.830	7.50	0.513	1.263	0.710

$[H_2O_2]$ = 0.160 mol/L; time = 4 h; temp = 95°C

Rg shows an increasing trend with increase in the concentration of acrylamide. The plot of log Rg versus log [AAM] (Fig. 2) was drawn and found to be proportional to the 1.11 power of the acrylamide concentration.

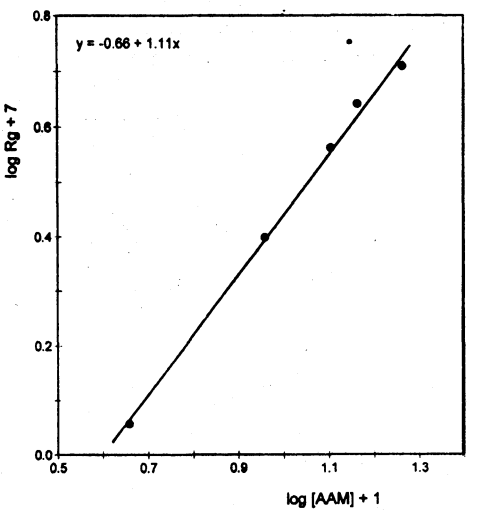

Fig. 2. Rates of grafting reactions *vs.* monomer concentration

Effect of Temperature on Rg: It was observed that from Table-3, Rg values steadily increased with increase in temperature. The energy of activation value (Ea) was determined from the plot log Rg versus 1/T (Fig. 3).

The calculated activation energy of grafting is for 70–95°C. In the first 4 h, at the temperatures under 70°C, no grafting was observed;, so grafting yields obtained for the temperatures 70, 85 and 95°C were used to calculate the overall activation energy.

TABLE-3
VALUES OF THE RATE OF GRAFTING (Rg) AT VARIOUS TEMPERATURES

Temp. (°C)	$1/T \times 10^3$	$Rg \times 10^6$ (mol/L s)	log [Rg] + 7	$k \times 10^6$ ($L^{0.75}/mol^{0.75}$ s)
70	2.914	0.233	0.368	2.37
85	2.792	0.461	0.664	4.69
95	2.716	0.513	0.710	5.21

$[H_2O_2]$ = 0.160 mol/L; [AAM] = 1.830 mol/L; time = 4 h

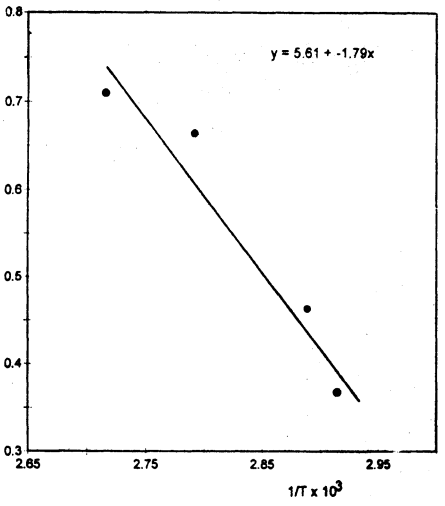

Fig. 3. Arrhenius plot of log Rg *vs.* 1/T for grafting of AAM upon PET using H_2O_2

Conclusions

Under the experimental results, a suitable grafting rate equation was proposed. The grafting rate equation of acrylamide onto PET fibres can be written as:

$$Rg = k[H_2O_2]^{0.64}[AAM]^{1.11}$$

As seen from the rate equation, the total degree of grafting is 1.75. The overall activation energy for grafting of AAM onto PET fibres by H_2O_2 was found to be 34.3 kJ/mol. As is seen from Table-3 overall rate constant increases with temperature similar to conventional chemical reactions.

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