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Kinetic Investigation of Grafting of Methylmethacrylate-Acrylic Acid Mixture onto Poly(ethylene terephthalate) Fibers with Benzoyl Peroxide

FARIBORZ AZIZINEZHAD*, ROMIC HARUTYUNYAN† and MAJID ABDOUSS‡
Department of Chemistry, Islamic Azad University, Varamin Branch, Varamin, Iran
Tel: (98)(291)2275805; E-mail: fazizinejad@yahoo.com

In this study the rate of grafting and some kinetic parameters of the graft copolymerization of (methylmethacrylate - acrylic acid) mixture onto poly(ethylene terephthalate) fibers with benzoyl peroxide was investigated. The rate of grafting was found to the 1.63 and 0.88 powers of monomer mixture and initiator concentrations, respectively. The activation energy (64.15 kJ/mol) of the reaction at four different temperature from 343 to 358 K, was calculated. As mentioned below, the use of anionic and cationic emulsifiers cause a decrease in graft product and on the other hand with the use of initiators mixture such as benzoyl peroxide and potassium persulphate (Bz_2O_2-KPS) the graft product has a decreased. However with the increase of graft, intrinsic viscosity increased and density decreased.

Key Words: Graft copolymerization, Methylmethacrylate, Acrylic acid, Benzoyl peroxide.

INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic fibers improve their properties. For example, the grafting of acrylamide[1], 4-vinyl pyridine[2], acrylic acid[3-5], 2-methyl-5-vinyl pyridine[6], methacrylic acid[7], methylmethacrylate[8,9] onto poly(ethylene terephthalate) fibers have been reported by researchers. The graft copolymerization of binary mixtures of vinyl monomers has special importance in comparison to simple grafting of individual monomers. This technique of grafting of monomer mixtures has the advantage of creating grafted chains with tailor-made properties for specific applications. The synergistic effect of the co monomer in grafting mixtures plays an important role in controlling the composition and graft yield onto poly(ethylene terephthalate)[10-12]. In our previous work optimum grafting conditions were obtained[10]: $[Bz_2O_2] = 4.0 \times 10^{-3}$ M, [monomer mixture] (AA 30 % + MMA 70 %) = 0.1 M, temperature = 358 K, time = 40 min.

The aim of this study is to determine the relation between the rate of grafting and the concentration of mixture of monomers and initiator and some kinetic parameters related to the grafting reaction. However the role of emulsifiers and initiators mixture in graft making has been investigated.

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†Department of Chemistry, Yerevan State University, Yerevan, Armenia.
‡Department of Chemistry, Amir Kabir University of Technology, Tehran, Iran.

EXPERIMENTAL

The multifilament poly(ethylene terephthalate) fibers (30 filaments) were cut in bundles of certain weights, Soxhlet-extracted with acetone for 6 h and dried at 323 K. Methylmethacrylate-acrylic acid (Merck, Germany) were used after purification. Acrylic acid (AA) was vacuum-distilled over a column filled with copper wires at 303 K. Methylmethacrylate (MMA) was washed three times with 5 % NaOH, dried over $CaCl_2$ and finally distilled in vacuum at 319 K. Benzoyl peroxide (Bz_2O_2) was recrystallized twice from the methanol-chloroform mixture and potassium per sulfate (KPS) was recrystallized five times with doubly distilled water and both of them dried in vacuum. All emulsifiers and solvents were supplied by Merck and doubly distilled water has been used in all experiments.

Grafting procedure: Grafting was carried out in 100 mL pyrex tubes. The polymerization tube containing the poly(ethylene terephthalate) fiber sample, monomer and 45 mL doubly distilled water was placed in water bath (Lauda D 40 S, Germany, ± 0.1 ºC) and kept there for 2 min and then 5 mL acetone containing appropriate amount of Bz_2O_2 was added. The fibers taken from the polymerization system after 15 min (before reaching saturation), washed with water at room temperature for 24 h, then Soxhlet extracted with benzene for 8 h. Finally, the sample was dried until it maintained a constant weight. The amount of graft added onto the fiber was determined gravime-trically. The per cent increase in fiber weight was taken as graft yield percent (G %) $G\ \% = \left(\frac{w_2 - w_1}{w_1}\right) \times 100$, where w_1 and w_2 were the weight of the original and grafted poly(ethylene terephthalate), respectively.

The rate of grafting was calculated with this equation: $R_g = \left(\frac{w_2 - w_1}{v.t}\right)$ where v is the volume of the solution (L) and t is the grafting time (S)[11].

Measurement of density: The densities of the fiber samples were measured by density gradient column at 296 K. The calibration of the column was made by the marker floats (Davenport Ltd.), their densities were determined with an accuracy of 1/10000. The levels of the marker floats and the fibers were measured using a cathetometer having a sensitivity of ± 0.01 mm with xylene and carbon tetrachloride. Results tabulated in Table-1. The fiber densities decreased with the increasing graft yield[7,9].

TABLE-1
DENSITY AND INTRINSIC VISCOSITY VALUES

Graft yield (%)	Density (g/cm^3)	Intrinsic viscosity (dL/g)
0.0	1.3735	0.085
19.0	1.3614	0.295
33.5	1.3485	0.578
45.0	1.3352	0.936
58.9	1.3216	1.327

This fact identified that the contribution of grafted side chains to the weight of fibers are less than their contribution to the volume of them. We suggest that the existing of MMA and AA groups in fibers may lead to dimensional difficults for packing of fibers and thus with the increase of graft yield the density would decrease.

Measurement of intrinsic viscosity: The intrinsic viscosity values of the ungrafted and grafted fibers were determined in *m*-cresol and ethanol at 298 K. Experiments were carried out by using a Ostwald viscometer having a solvent flow time 185 s. Results tabulated in Table-1.

Determination of the intrinsic viscosity for different samples was solved by Huggins equation:

$$\eta_{sp}/C = [\eta] + k[\eta]^2 \cdot C$$

The extrapolation of the curve of $\eta_{sp}/C - C$ identified the intrinsic viscosity[8]. The intrinsic viscosity was shown an increasing depend on the graft yield[1,2,8].

Effect of different emulsifiers: The grafting procedure was carried out in the presence of different emulsifiers [sodium lauryl sulphate (SLS), dodecyltrimethyl ammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB)]. Experiments did in fix condition ([MMA/AA] = 70/30 = 0.1 M, $[Bz_2O_2] = 4.0 \times 10^{-3}$ M, T = 358 K, t = 40 min, emulsifier = 2 %).

Results showed that decreasing in the graft yield in the presence of DTAB, CTAB, (DTAB/CTAB = 1/1) and SLS, from (58.9 % in emulsifier free fiber) to 5.57, 3.00, 2.25 and 1.70 %, respectively. It seems that emulsifiers have terminating effect upon the PET macro radical and graft chain radicals and reaction of the initiator radical with emulsifier molecule cause decrease the number of active free radical sites on the PET. On the other hand, homo polymerization reactions occurs faster than grafting reactions.

Effect of different initiators: With the use of potassium per sulfate and benzoyl peroxide initiators and their mixtures at the firm condition of, T = 358 K, time = 40 min, [M] = (AA 30 % + MMA 70 %) = 0.1 M the graft copolymerization has been done. Table-2 shows that potassium per sulfate would cause the solution homo polymerization and insignificant graft product, because the potassium per sulfate itself is a reductive initiator and before affecting on the PET fiber chains would be decomposed in the water. During the use of (KPS)/(Bz_2O_2) mixture, because of

TABLE-2
EFFECT OF DIFFERENT INITIATORS

$C \times 10^3$ (M)	G % (Bz_2O_2)	G % (KPS)	$C \times 10^3$ (M)	G % (Bz_2O_2/KPS)
1	19.70	0.65	1/3	9.15
2	34.45	0.85	2/2	22.81
3	44.43	1.05	3/1	29.28
4	58.90	1.37	-	-

rapid homo polymerization production in solution, the graft production will be lower than solely use of (Bz_2O_2), therefore (KPS) initiator even in mixture with the free radical initiators is not optimum for graft product.

RESULTS AND DISCUSSION

Kinetics of grafting: The number of studies concerning the grafting of vinyl monomers onto PET fibers using Bz_2O_2 is quite limited. The grafting of methylmethacrylate-acrylic acid mixture onto PET fibers using this initiator was reported[10].

In a study where a monomer is grafted onto PET fibers inevitably homo polymer of the monomers is obtained together with the grafted fibers. Therefore the monomer in the medium is used in both the grafting and homo polymer formation processes. The relation between the rate of grafting and the monomer and initiator concentrations can be writhen as:

$$R_g = k\,[I]^m\,[M]^n$$

here m and n can be determined by the logarithmic form of the equation:

$$\log R_g = \log k + m \log [I] + n \log [M]$$

[I] = initiator concentration, [M] = monomer concentration. The experimental data obtained at the 15th minute of polymerization (before reaching saturation), related to the change in the graft yield with the initiator concentration keeping the concentration of monomer mixture constant are tabulated in Table-3. and these data were used to plot $\log R_g + 4$ *versus* $\log [Bz_2O_2] + 4$. The slope of the graph showed that the rate of grafting was 0.88-order with respect to the Bz_2O_2 concentration (Fig. 1).

TABLE-3
DEPENDENCE OF THE RATE OF GRAFTING ON Bz_2O_2 CONCENTRATION
[MMA/AA] (AA 30 % + MMA 70 %) = 0.1 M, t = 15 min, T = 358 K

$[Bz_2O_2] \times 10^3$ (M)	G (%)	$R_g \times 10^4$ (mol/L.S)	$\log [Bz_2O_2] + 4$	$\log R_g + 4$
0.5	3.33	2.22	0.70	0.34
1.0	6.67	4.44	1.00	0.65
2.0	13.30	8.87	1.30	0.95
4.0	20.00	13.33	1.60	1.12

The slope of the $\log R_g$ *versus* log [MMA/AA] graph plotted using the data in Table-4 at the 15th minute showed that the rate of grafting was proportional to the 1.63 power of the monomer mixture concentration (Fig. 2).

TABLE-4
DEPENDENCE OF THE RATE OF GRAFTING ON MONOMER MIXTURE CONCENTRATION, $[Bz_2O_2] = 4.0 \times 10^{-3}$ M, t = 15 min, T = 358 K

MMA/AA (AA 30 % + MMA 70 %) (M)	G (%)	$R_g \times 10^4$ (mol/L.S)	log [MMA/AA] + 3	$\log R_g + 4$
0.025	2.00	1.33	1.40	0.12
0.050	5.00	3.33	1.70	0.52
0.075	11.66	7.77	1.87	0.89
0.100	18.33	12.22	2.00	1.08

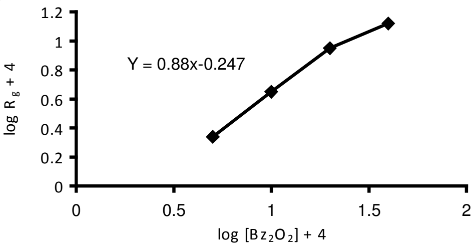

Fig. 1. Rate of grafting reaction-Bz_2O_2 concentration

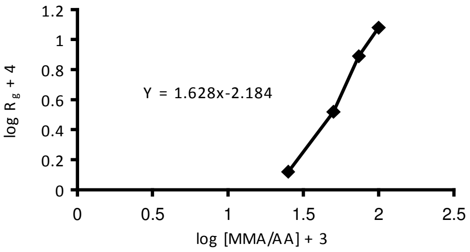

Fig. 2. Rate of grafting reaction-(AA 30 % + MMA 70 %) concentration

The overall activation energy for grafting was determined from Arrhenius plot of log R_g *versus* 1/T (Fig. 3). The overall activation energy for grafting was determined to be 64.15 kJ/mol. Results tabulated in Table-5.

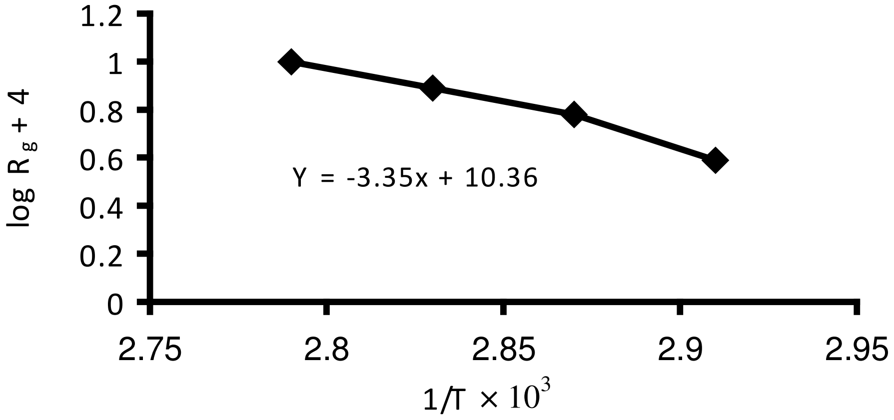

Fig. 3. Arrhenius plot of log R_g-1/T

TABLE-5

VVALUES OF THE RATE OF GRAFTING AT VARIOUS TEMPERATURES

$[Bz_2O_2] = 4.0\times10^{-3}$M, [MMA/AA] (AA 30 % + MMA 70 %) = 0.1 M, t = 60 min

T (K)	1/T × 10^3	G (%)	$R_g \times 10^4$ (mol/L.S)	log R_g + 4
343	2.91	23.30	3.89	0.59
348	2.87	26.66	6.12	0.78
353	2.83	46.70	7.78	0.89
358	2.79	60.00	10.00	1.00

The surface morphology of fibers at different grafting yield was studied by JEOL-JEM-100 CX II microscope. As shown in Figs. 4-6 the degradation or deformation of fibers were not observed. But homogeneity of the surface decreased. The grafting can be shown by black point in fibers structure.

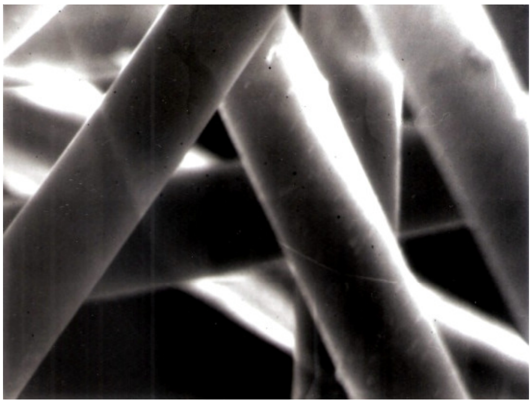

Fig. 4. SEM micrograph of AA grafted PET fibers at a magnification of × 1000 (3.7 %)

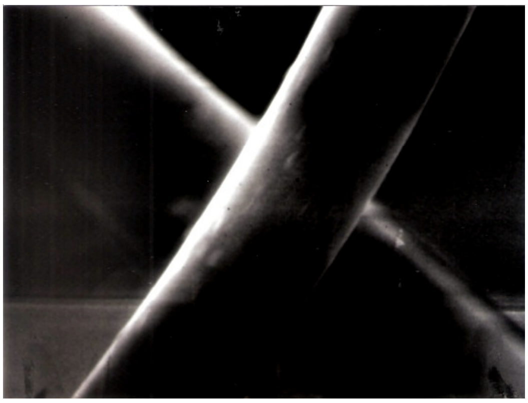

Fig. 5. SEM micrograph of MMA grafted PET fibers at a magnification of × 1000 (30.0 %)

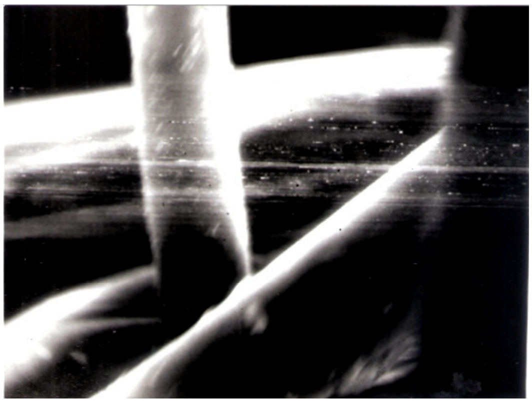

Fig. 6. SEM micrograph of (MMA-AA) mixture grafted PET fibers at a magnification of × 1000 (58.9 %)

Conclusion

Experimental results showed, the grafting rate equation of methylmethacrylate-acrylic acid mixture onto PET fibers can be written this form:

$$R_g = k[Bz_2O_2]^{0.88}[M]^{1.63}$$

Total degree of grafting is 2.51.

• The overall activation energy for grafting of MMA/AA onto PET fibers by Bz_2O_2 was found to be, 64.15 kJ/mol. In grafting of MMA and AA onto PET fibers (without co-monomer) the values of activation energy were determined 101.36 and 41.38 kJ/mol respectively[5,9].

• On the other hand the effect of 2 % anionic and cationic emulsifiers showed a decreasing in the graft yield as follows:

$$\text{DTAB} < \text{CTAB} < \text{DTAB/CTAB} < \text{SLS}$$

• The effect of reductive and free radical initiators may cause the decrease of graft product and the rate of homo polymerization regarding to copolymerization has an increase.

• Densities decreased with the increasing graft yield, while the intrinsic viscosity showed an increasing with the graft yield. The micrographs showed that there were the black points in fibers structure. These results confirmed the grafting of fibers.

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