Kinetic Investigation of Grafting of Acrylic Acid/2-Hydroxypropyl Methacrylate Mixture onto Poly (Ethylene Terephthalate) Fibers

Fariborz Azizinezhad, Arash Borzou, Mohsen Shabani

***Abstract*— In this study, the chemical grafting of acrylic acid/2-hydroxypropyl methacrylate (AA/2-HPMA) mixture and the rate of grafting onto poly (ethylene terephthalate) (PET) fibers using benzoyl peroxide (Bz_2O_2) was investigated. The thermogravimetric analysis (TGA) results displayed that the decomposition temperature of the fibers decreased with grafting. Scanning electron microscopy (SEM) images comfirmed that the grafting changed the surface morphology of the fibers and a shell-like heterogeneous structure observed as a result of grafting. The rate of grafting was calculated to be proportional to the 0.6 and 0.63 powers of monomer mixture and initiator concentrations, respectively. The overall rate activation energy at the range of 338-363K was calculated 37.53 kJ / mol.**

***Index Terms*— Poly (ethylene terephthalate), grafting, benzoyl peroxide, kinetics**

I. INTRODUCTION

PET fibers have a prominent place among synthetic fibers.Due to lack of the reactive functional groups in PET structure it must be modified by different methods. Grafting is one of the most important methods for modification of PET fibers. [1-17] There are many researches on the grafting of monomer or monomer mixtures onto PET fibers by chemical or radiation methods. [5-15] In our previous work, the best condition of the grafting of AA/2-HPMA mixture were determined: ([Bz_2O_2 = 4.0 × 10^{-3}M , [AA/2-HPMA] (20%AA+80%2-HPMA) = 0.2 M , T = 363K and time = 60 min. [16] The aim of this research was to determine of the relation between the rate of grafting and the concentration of the monomer mixture and initiator as well as overall activation energy.

II. MATERIALS AND METHODS

A. Experimental

The multifilament PET fibers (stretch ratio 2, 30 filaments, 110 dTex) were purchased from Amir Kabir University and Technology (Iran). They were cut in bundles (0.15±0.01g) and after soxhlet – extracted with acetone for 6h and drying in oven at 50C were used.Both of monomers were bought from Merck. Co (Germany) and after purification by vacuum distillation were used. Bz_2O_2 (Merck) was recrystallized twice from the mixture of methanol-chloroform and dried in a vacuum dessicator. All solvents and reagents were analytical grade and supplied by Merck and doubly distilled water was used in all experiments.

B. Grafting procedure and kinetic investigation

Grafting was carried out in a 100 ×10^{-3} mL Pyrex tube. The polymerization tube containing the PET fiber specimen (0.15±0.01g) , appropriate amount of the monomer mixture and 18×10^{-3} mL doubly distilled water was placed in water bath(Lauda D40S , Germany) , and kept there for 2 minute. Then 2 ×10^{-3} mL acetone containing the required concentration of Bz_2O_2 was added. The volume of the mixture was placed into a water bath at the fix polymerization temperature. After desirable time, the fiber specimen was taken out. The removal of undesirable homopolymers and solvent were accomplished with doubly distilled water and Soxhlet-extracted with toluene-acetone mixture for 8 and 24 hour, respectively. The sample was dried in vacuum at 50C. Then the percentage of grafting (G%) was computed as follows:

$$G(\%) = \frac{W_g - W_0}{W_0} * 100 \qquad (1)$$

Where, W_g and W_0 are the weights of the grafted and ungrafted PET, respectively.
By the help of the following equations the rate of grafting was calculated: [9,17]

$$R_g = \frac{(W_g - W_0)}{V\,t} \qquad (2)$$

$$R_g = k[I]^m[M]^n \qquad (3)$$

Where, V is the volume of the solution (L) and t is the grafting time (S).On the other hand, m and n can be determined by the logarithmic form of above equation:

$$\log R_g = \log k + m\log[I] + n\log[M] \qquad (4)$$

C. Characterization methods

The SEM micrographs of grafted and ungrafted fibers, coated with gold, were performed using a Philips XL30 scanning electron microscope. Thermogravimetric analysis of the fibers were carried out with Universal V4.1D TA Instruments in Helium atmosphere at the flow rate of 200 mL/min between 25-800C at a heating rate of 10C.

Manuscript received September 20, 2014.
Fariborz Azizinezhad, Department of Chemistry, College of Science, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran, +989127216112
Arash Borzou, Department of Agronomy, College of Agriculture,Varamin – Pishva Branch, Islamic Azad University, Varamin, Iran, +989126177928
Mohsen Shabani, Department of Chemistry, College of Science, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran, +989122079144

III. RESULTS AND DISCUSSION

A. *Kinetics of grafting*

The relation of the rate of grafting reaction to the change of monomer mixture and initiator concentrations at the 15th minute of polymerization (before reaching saturation), were determined .The results of the variation of the monomer mixture concentration from 0.05 mol/L to 0.2 mol/L at the firm condition of other variables were determined the order of reaction respect to monomers. Relation of the log R_g+4 vs log [AA/2-HPMA] +3 are tabulated in Table 1. The slope of the graph distinguished that the rate of grafting was 0.60-order with respect to the monomer mixture. Fig. 1. The results of the variation of the initiator concentration from 1.0×10^{-3} mol/L to 4.0×10^{-3} mol/L at the fixation condition of other variables were ascertained the order of reaction respect to initiator. Relation of the log R_g+ 4 vs log [Bz_2O_2] +4 in the above range are tabulated in Table 2. The slope of the graph specified that the rate of grafting was 0.63 -order with respect to the Bz_2O_2. Fig. 2. Therefore, the grafting rate can be written as:

$R_g = k\,[\text{initiator}]^{0.63}\,[\text{monomers}]^{0.60}$

The overall activation energy for grafting was calculated from Arhenius plot of logR_g vs 1/T at four different temperatures from 338K to 363K in 60 min. Table 3 and Fig. 3 showed that the overall activation energy was 37.53 kJ / mol.

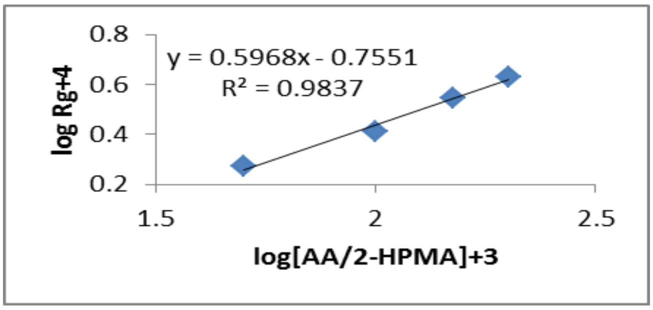

Fig. 1. Rate of grafting reaction vs. (AA 20% / 2-HPMA 80%) concentration

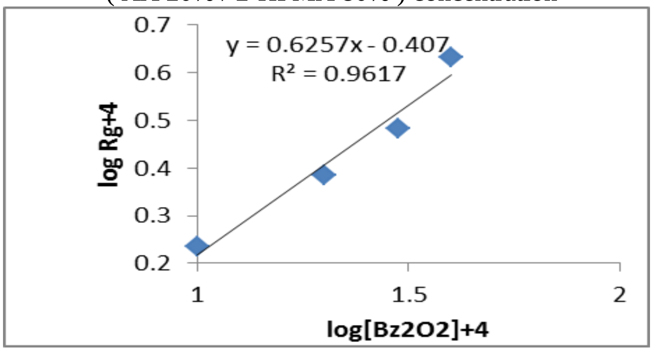

Fig. 2. Rate of grafting reaction vs. Bz_2O_2 concentration

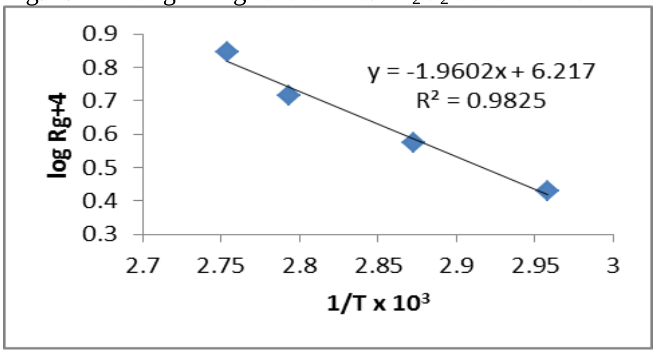

Fig. 3. Arrhenius plot of log R_g vs.1/T

Table1. Dependence of the rate of grafting on monomer mixture concentration

([Bz_2O_2] = 4.0×10^{-3}mol/L, t =15 min, T=363K)

[AA/2-HPMA] (mol/L)	G (%)	$R_g\times10^4$ (mol/L.S)	Log[AA/2-HPMA]+3	logR_g+4
0.05	11.25	1.875	1.699	0.273
0.10	15.45	2.575	2.000	0.410
0.15	21.00	3.500	2.176	0.544
0.20	25.75	4.291	2.301	0.632

Table 2. Dependence of the rate of grafting on initiator concentration ([AA/2-HPMA] (AA20%+2-HPMA80%)= 0.2 mol/L, t =15 min, T=363K)

[Bz_2O_2]× 10^3 (mol/L)	G (%)	$R_g\times10^4$ (mol/L.S)	Log [Bz_2O_2]+4	logR_g+4
1	10.35	1.725	1.000	0.236
2	14.60	2.433	1.301	0.386
3	18.30	3.050	1.477	0.484
4	25.75	4.291	1.602	0.632

Table 3. Values of the rate of grafting at different temperatures ([Bz_2O_2]= 4.0×10^{-3} mol/L,[AA/2-HPMA] (AA 20%+2-HPMA 80%) = 0.2 mol/L,t=60min

T(K)	G (%)	$R_g\times10^4$ (mol/L.S)	$1/T\times10^3$	logR_g+4
338	16.20	2.700	2.958	0.431
348	22.45	3.741	2.873	0.573
358	31.20	5.200	2.793	0.716
363	42.00	7.000	2.754	0.845

B. *Characterization of the fibers*

As shown in Figs. 4 and 5 with an increase in grafting yield, the fibers structure showed a heterogeneous structure and their surfaces observed so rough. [9,13] TGA data showed that, the decomposition temperature of the fibers decreased after modifying Fig 6. All of these results confirm that, the grafting of monomer mixture onto PET backbone. [11,14]

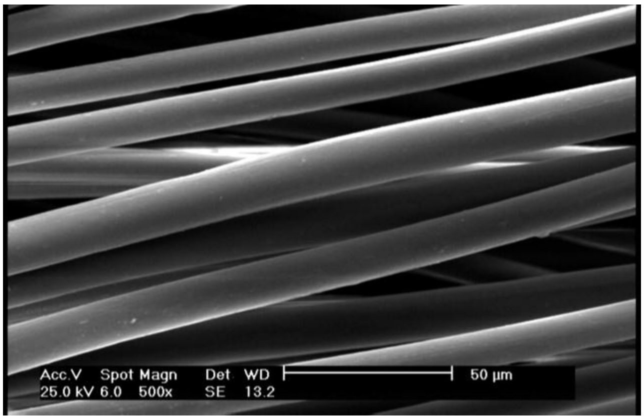

Fig. 4. SEM micrograph of ungrafted PET fiber

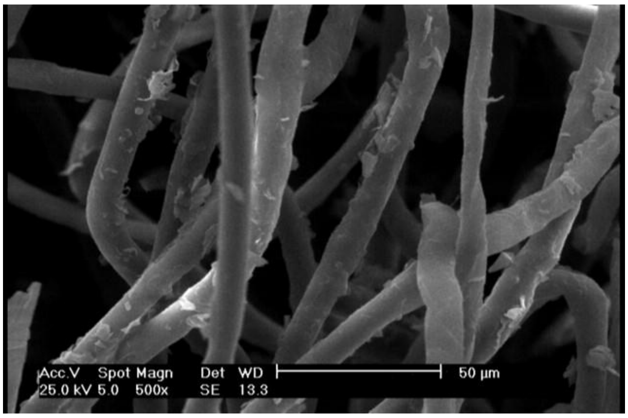

Fig. 5. SEM micrograph of AA/2-HPMA mixture onto PET

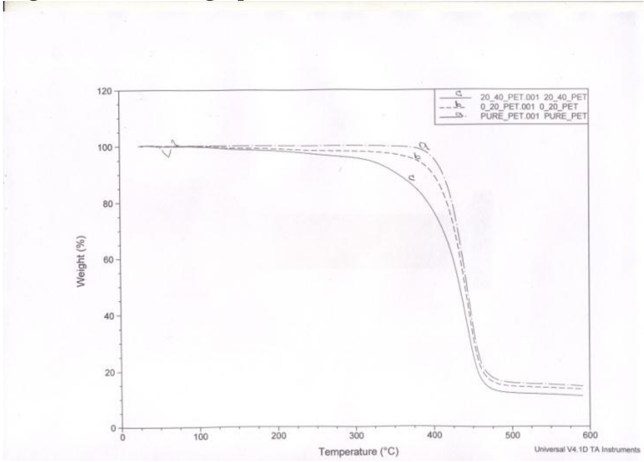

Fig. 6. Thermograms of (a) ungrafted, (b,c) (14.60% , 31.20% grafted) onto PET fibers.

IV. CONCLUSION

The experimental results showed that, the using of the monomers concurrently causes a synergistic effect on the grafting yield. It was showed that, the rate of grafting was found to 0.60 powers of monomers and 0.63 of initiator, respectively. Therefore, the total degree of grafting is 1.23.The overall activation energy for grafting was calculated as 37.53 kJ/mol.

REFERENCES

[1] O. Sanli, E. Pulat., Solvent-assisted graft copolymerization of acrylamide on poly(ethylene terephthalate) films using benzoyl peroxide initiator J.Appl.Polym.Sci 1993 (47) pp. 1-6.

[2] F. Osipenko., V.I Martinovicz., Grafting of the acrylic acid on poly (ethylene terephthalate) J. Appl. Polym. Sci, 1990 (39) pp. 935-942.

[3] M. Sacak., F. Oflaz., Benzoyl-peroxide-initiated graft copolymerization of poly(ethylene terephthalate) fibers with acrylic acid J. Appl. Polym. Sci, 1993 (50) pp. 1909-1916.

[4] E.M. Abdel-bary., A.A Sarhan., H.H. Abdel-razik., Effect of graft copolymerization of 2-hydroxyethyl methacrylate on the properties of polyester fibers and fabric J. Appl. Polym. Sci, 1988 (35), pp. 439-448.

[5] F. Azizinezhad., Kinetic investigation of grafting of poly (ethylene terephthalate) fibers with 2-hydroxypropyl methacrylate using 4,4-azobis(4-cyanovaleric acid), Asian. J. Chem, 2011 (23)(2), pp.809-902.

[6] F. Azizinezhad., Grafting of 2-hydroxypropyl methacrylate onto poly(ethylene terephthalate) fibers and dyeability, Asian. J. Chem, 2011, (23)(2), pp.839-842.

[7] M. Okoniewski., J. Sogka., S. Ledakovicz., Chemically induced graft copolymerization of acrylic acid onto polyester fabrics. I. Kinetic investigation of grafting, J. Appl. Polym. Sci, 1988 (35), pp. 1241-1249.

[8] M. Sacak., N. Bastug., M. Talu., Azobisisobutyronitrile-Initiated graft copolymerization of methyl methacrylate onto poly(ethylene terephthalate) fibers, J. Appl. Polym. Sci, 1993 (50), pp. 1123-1129.

[9] M. Arslan., M. Yigitoglu., O. Sanli., H.I. Unal., Kinetics of swelling assisted grafting of 4-vinyl pyridine onto poly(ethylene terephthalate) fibers using a benzoyl peroxide initiator Polym. Bull, 2003 (51), pp. 237-244.

[10] A. Hebeish., S. Shalaby., A. Bayazeed., H_2O_2-induced graft polymerization of acrylic acid/styrene mixtures on poly(ethylene terephthalate) fibers J. Appl. Polym. Sci, 1982 (27), pp. 197-209.

[11] M. Celik., M. Sacak., Grafting of acrylamide–methacrylic acid mixture onto poly(ethylene terephthalate) fibers by azobisisobutyronitrile J. Appl. Polym. Sci, 1996 (59), pp. 609-617.

[12] F. Azizinezhad., M. Talu., M. Abdouss., M. Shabani., An Investigation of the Grafting of Acrylic Acid/Methyl Methacrylate Mixture onto Poly(ethylene terephthalate) Fibres Iran. Polym. J, 2005 14(1), pp. 33-38.

[13] m. Arslan., kinetics of graft copolymerization of acrylamide and 2-hydroxyethylmethacrylate monomer mixture onto poly (ethylene terephthalate) fibers ,korean. J .chem., 2010 (27)(3), pp .991-998.

[14] H. Ahmadpanahi., M. Abdouss., F. Ghiabi., E. Moniri., A.M .Shoushtari., Modification and characterization of poly (ethylene terephthalate)-grafted-acrylic acid/acryl amide fiber for removal of lead from human plasma and environmental samples, J. Appl. Polym. Sci , 2012 (124) , pp .5236-5246.

[15] M. Abdouss, H. Ahmadpanahi., E. Moniri., A.M. Shoushtari., Modification of Poly(Ethylene Terephthalate) Fiber by Grafting of Acrylic Acid/Acrylamide for Removal of Pb^{+2} from Aqueous Solutions , Iran J Chem Eng , 2012 (31)(1) , pp. 15-21.

[16] F. Azizinezhad., Free radical grafting of 2-hydroxypropyl methacrylate/acrylic acid mixture onto poly (ethylene terephthalate) fibers, Eur. J. Experimental. Biology, 2014 (4)(1), pp. 560-567.

[17] F. Azizinezhad., R. Harutyunyan, M. Abdouss, Kinetic investigation of grafting of methylmethacrylate-acrylic acid mixture onto poly(ethylene terephthalate) fibers with benzoyl peroxide, Asian. J. Chem, 2010 (22)(10), pp.7803-7809.


Dr. Fariborz Azizinezhad is assistant professor at Islamic Azad university of Varamin-Pishva Branch. He has about 25 articles in polymer synthesize and kinetics, surface adsorption and surface chemistry.


Dr. Arash Borzou is assistant professor at Islamic Azad university of Varamin-Pishva Branch. He has about 6 articles in polymer synthesize and kinetics, surface adsorption and soil chemistry.


Dr. Mohsen Shabani is assistant professor at Islamic Azad university of Varamin-Pishva Branch. He has about 17 articles in polymer synthesize and kinetics, computational chemistry, surface adsorption and surface chemistry.