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ORIGINAL ARTICLE

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

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ABSTRACT

The graft copolymerization of acrylamide/2-hydroxypropyl methacrylate (AAm/2-HPMA) onto poly (ethylene terephthalate) fibres was studied using benzoyl peroxide(Bz_2O_2) as an initiator. The use of 2-HPMA as a comonomer increased the amount of AAm introduced to the PET fibre up to 46% while the grafting of AAm onto fibres alone gave low graft yields(8.8%). This synergistic effect was found to be at its highest when an AAm/2-HPMA mixture having 20% AAm (wt.) was used. The grafting improved the antibacterial and the moisture regain of the fibers. Effect of different parameters, such as initiator and monomers concentration, reaction time and temperature were studied. Optimum condition for grafting were determined to be [Bz_2O_2] = 4.0×10^{-3} mol/dm^3, [AAm / 2-HPMA] = 0.2 mol/dm^3, T =90°C, t =60 min. The rate of grafting was calculated to the 0.57 power of monomer mixture and 0.61 power of initiator. The overall activation energy for grafting was ascertained as 27.84 kJ / mol. The grafted fibers were characterized by thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR)
Keywords: *Poly (ethylene terephthalate), grafting, benzoyl peroxide*

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INTRODUCTION

Poly (ethylene terephthalate) (PET) structure is hydrophobic and high crystalline in nature and do not contain chemically reactive groups. Graft copolymerization is one of the best methods for improving of undesirable properties of PET. Vinyl graft copolymerization onto PET fibers could be initiated by chemical or radiation methods. [1-20] Chemical methods have more advantageous as regardation of the main polymer. The grafting of monomer mixture onto PET fibers generally results in a synergistic effect. There are a few researches on the grafting of monomer mixture onto PET Fibers. [12-20] The graft copolymerization of AAm [1,2] and 2-HPMA[6,7] individually onto PET was reported, but using a binary mixture of (2-HPMA/AAm) is not available in the literature. This article reports the grafting of 2-HPMA/AAm mixture onto PET fibers by the use of Bz_2O_2. The characterizations of grafted PET fibers were investigated by TGA, SEM and FTIR spectroscopy.

EXPERIMENTAL

Materials

The PET fibers (stretch ratio 2, 30 filament, 110 dTex) were provided by Amir Kabir University and Technology(Iran). They were cut as small hank (0.15±0.01g) soxhlet – extracted with acetone and dried at 50°C. 2-HPMA was purchased by Merck (Germany) and after purification by vacuum distillation were used.AAm (Aldrich) was recrystallized from chloroform solution , washed with dry benzene and dried for 24 h under vacuum. Bz_2O_2 (Merck) was recrystallized twice from the mixture of methanol-chloroform and dried in a vacuum dessicator. All solvents and reagents were supplied by Merck and doubly distilled water was used in all experiments

Grafting procedure

Grafting was carried out in a 100 ×10^{-3} dm^3 pyrex tube. The polymerization tube containing the PET fiber specimen (0.15±0.01g) , appropriate amount of the monomer mixture and 18×10^{-3} dm^3 doubly distilled water was placed in water bath(Lauda D40S , Germany) , and kept there for 2 minute. Then 2 ×10^{-3} dm^3 acetone containing the required concentration of Bz_2O_2 was added. The volume of the mixture was placed into a water bath at the firm 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 50°C. Then the percentage of grafting (G%) was computed as follows:

1) $G(\%) = (W_g - W_0) / W_0 \times 100$

Where, W_g and W_0 are the weights of the grafted and ungrafted PET, respectively.

By the help of the following equation the rate of grafting was calculated: [6, 16]

$R_g = (W_g - W_0) / V.t$ 2)

where, V is the volume of the solution (dm^3) and t is the grafting time (S).

Determination of moisture regain and diameter

The PET fibers with different percents of graft yield were immersed in 65% sulphuric acid with density of 1.275 $g/10^{-3}dm^3$ for 24 h. Then they were oven dried at 100°C and were kept in desiccators over P_2O_5 for 1 h and weighted. The percentage of moisture regain was computed as follows:

3) Moisture regain (%) = $(M_n - M_0) / M_0 \times 100$

Where, M_n and M_0 denote the weights of fibers in wet environment and dry fibers, respectively. The fibers diameters were measured in three different regions by a Kyowa Microlux-11 microscope at a magnification of 1000×.

Antibacterial test

The antibacterial properties of the grafted fibers were evaluated by agar diffusion method. [21]For this aim, Escherichia coli was cultivated in a nutrient broth for 24 h in a CO_2 incubator. The grafted fibers (42.0%) were sterilized in an autoclave. The diluted bacteria suspension was cultured in a vial containing 0.15 g of the fibers. The vial was incubated at 37° C for 24 h. The bacteria collected from vial and plated on to the agar medium. After incubation at 37° C for 24 h, the bacterial colonies were observed visually.

Characterization methods

The FTIR spectra of 2-HPMA/AA grafted PET fibers were recorded using a Bruker Equinox FTIR spectrophotometer with KBr disks. The SEM photographs of grafted and ungrafted fibers, coated with gold, were accomplished using a Philips XL30 scanning electron microscope. Thermogravimetric analysis of the fibers were carried out with TGA V5.1A Dupont in helium atmosphere at the flow rate of 200 mL/min between 25-800°C at a heating rate of 10°C.

RESULTS AND DISCUSSION

The effect of monomer mixture ratios on the grafting

Investigation of the effect of monomer mixture ratios on the grafting was carried out at different wt% ratios of AAm and 2-HPMA. As shown in Fig.1, when AAm was grafted onto PET fibers, the maximum grafting yield was reached to 6.8%. The use of 2-HPMA as an individual monomer showed 23.5% grafting percentage. The grafting yield was extensively depend on the monomer mixture ratio, and the best condition was recorded (46.0%) at a (20%AAm+80%2-HPMA). [13-14]

Effect of initiator concentration

With an increase in the initiator concentration from 1.0×10^{-3} to 4.0×10^{-3} mol / dm^3 the grafting yield increased. This is attributed to increasing of the number of radicals and the active sites in PET structure. Although, the excess increase in the initiator causes increase in the growing polymer chains and combination reactions and as a resultant of these reactions, the percentage of grafting decreases. Other researchers were reported the same results. [13, 14] Fig.2

Effect of time and temperature

The results of the effect of temperature and time on the percentage of grafting were shown in **Fig.3** As shown in this figure, by increasing of the temperature (higher than glass transition of PET) and time, the flexibility, swell ability and of the PET chains increase. The optimum time for grafting was recorded 60 min. After this time, due to homopolymerization reactions in solution the viscosity of system was increased and this was made an inhibiting effect for diffusion of active radicals onto PET chains. [1, 2, 10]

Moisture regain and diameter

With an increase in the grafting yield, the water absorption capacity increased and at 46.0% of grafted fiber, it reached to 2.18%. This is attributed to the hydrophilic groups of –OH and $–CONH_2$ in 2-HPMA and AAm structures which grafted to PET backbone.[14 , 15]

The diameter of PET fibers showed an increasing from 1.44×10^{-2} mm (ungrafted fiber) to 2.12×10^{-2} mm (grafting percentage 46.0%)

The results of moisture regain and diameter are tabulated in **Table.1**

Mechanical properties of fibers

Instron vibromat set was used for determination of the mechanical properties, such as tensile strain and tenacity. In all experiments, the distance of jaws in phonograph was selected 20 cm and the rate of

elongation was 20 mm/min. The results of the mechanical properties were presented in **Table.2.** Some reductions in mechanical properties were observed, but these quantities are still acceptable. [20]

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/dm^3 to 0.2 mol/dm^3 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 [AAm/2-HPMA] +3 are tabulated in table 3. The slope of the graph distinguished that the rate of grafting was 0.57-order with respect to the monomer mixture. Fig4. The results of the variation of the initiator concentration from 1.0×10^{-3} mol/dm^3 to 4.0×10^{-3} mol/dm^3 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 4. The slope of the graph specified that the rate of grafting was 0.61 -order with respect to the Bz_2O_2. Fig 5. Therefore, the grafting rate can be written as: R_g= k [initiator] $^{0.61}$ [monomers] $^{0.57}$

The overall activation energy for grafting was calculated from Arhenius plot of the logR_g vs 1/T at four different temperatures from 338K to 363K in 60 min. Table 5 and Fig 6 showed that the overall activation energy was 27.84 kJ/mol.

Antibacterial activity

As shown in **Fig. 7** in the presence of the grafted fibers, growing of the Escherichia coli was decreased. This is attributed to the positively charged amino group which interacts with negatively charged microbial cells, leading to the leakage of proteinaceous and other ingredients of the microorganisms.

Characterization of the fibers

The results obtain from FTIR spectrum of grafted PET fibers showed some changing as regards to ungrafted PET. The adsorption bands at 2965 cm^{-1} and 1091 cm^{-1}are related to alcoholic –OH group of 2-HPMA and 2074 cm^{-1} amidic –NH_2 group of AAm, respectively. These new peaks confirm that, the PET fibers were grafted by both of monomers. [7, 15] **Figs. 8, 9.** As shown in **Figs .10, 11**, with an increase in grafting yield, the fibers structure showed a heterogeneous structure and their surfaces observed so rough. [7, 11] TGA data showed that, the decomposition temperature of the fibers decreased after modifying. The thermal decomposition temperature of raw PET (395°C) was decreased to (335°C) at 46.0% grafted yield. **Figs. 12, 13.** All of these results confirm that, the grafting of monomer mixture onto PET backbone. [13-17].

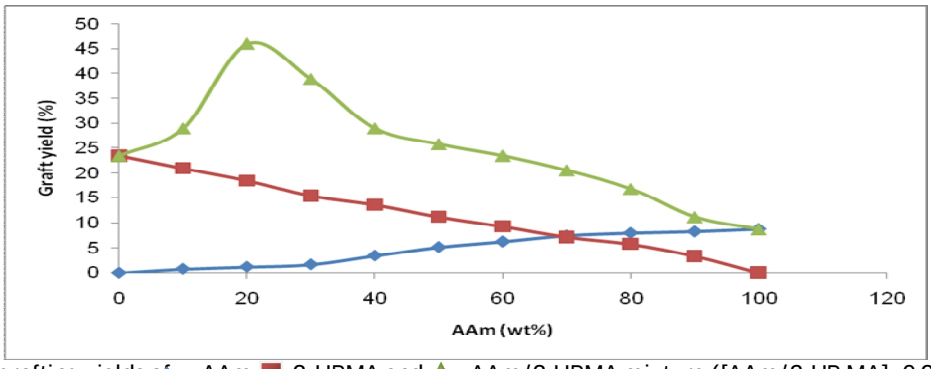

Fig1. The grafting yields of AAm, 2-HPMA and AAm/2-HPMA mixture ([AAm/2-HP MA]=0.2mol/dm^3, Time=2h , Temperature=90°C , [Bz_2O_2]=4.0×10^{-3}mol/dm^3)

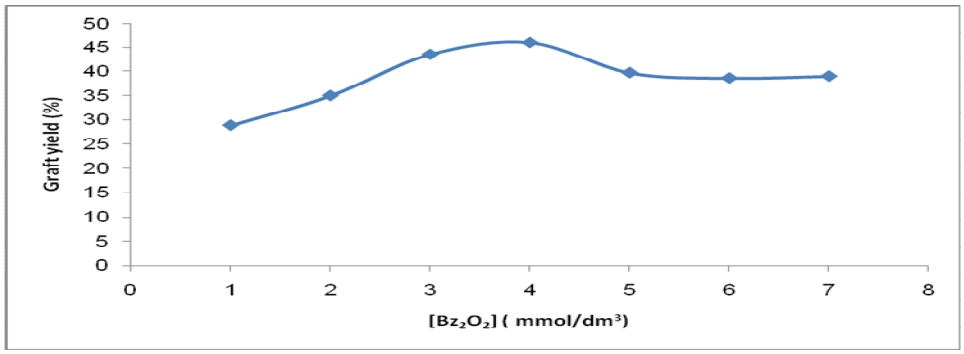

Fig2. Effect of Bz_2O_2 concentration on the grafting yield ([AAm/2-HPMA] (20 wt% AAm) = 0.2mol/dm^3 , Time =2h , Temperature = 90°C)

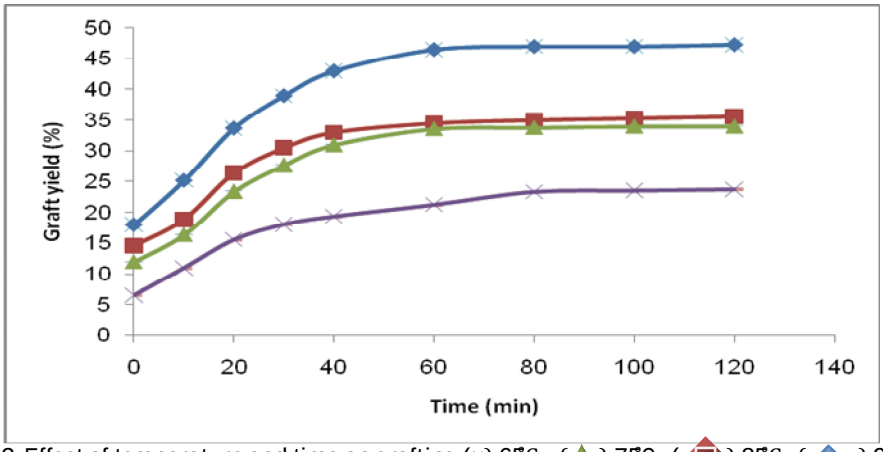

Fig3. Effect of temperature and time on grafting (×) 65°C , (▲) 75°C , (◆) 85°C , (◆) 90°C
([AAm/2-HPMA] (20 wt% AAm) =0.2mol/dm³ , Time=2h , Temperature=90°C , [Bz_2O_2]=4.0×10⁻³mol/dm³)

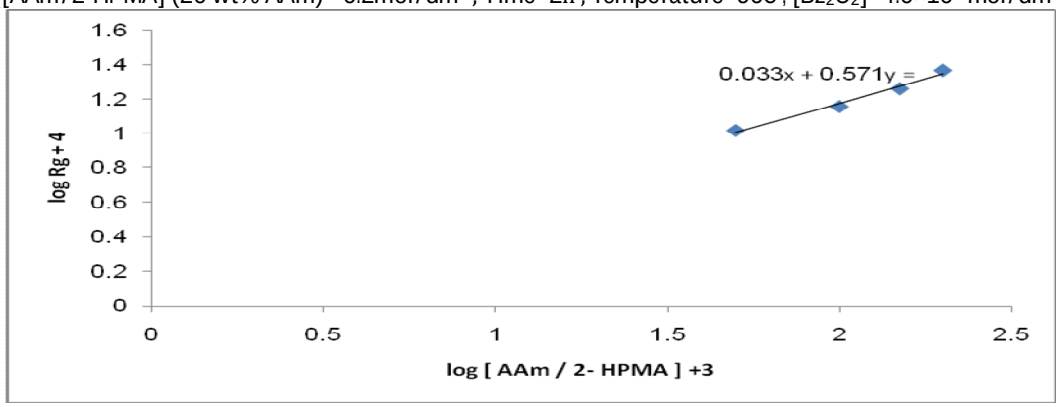

Fig 4.Rate of grafting reaction – (AAm 20% / 2-HPMA 80%) concentration

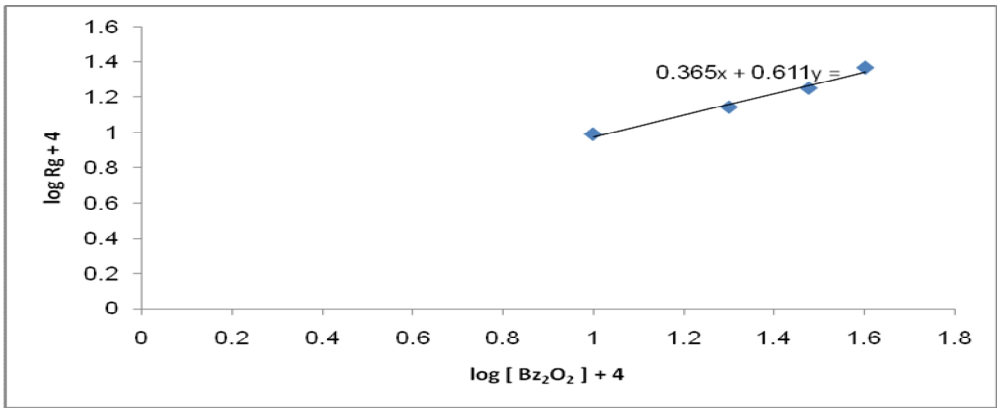

Fig5. Rate of grafting reaction – Bz_2O_2 concentration

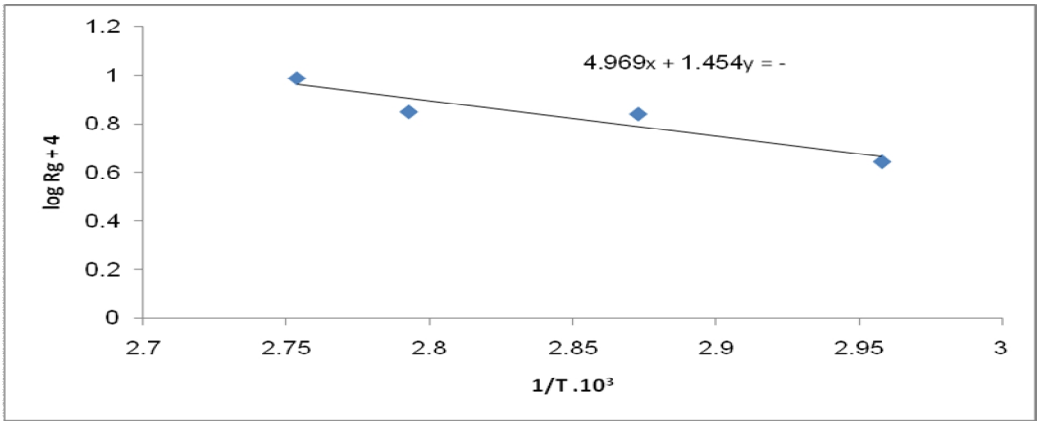

Fig6. Arrhenius plot of log R_g – 1/T

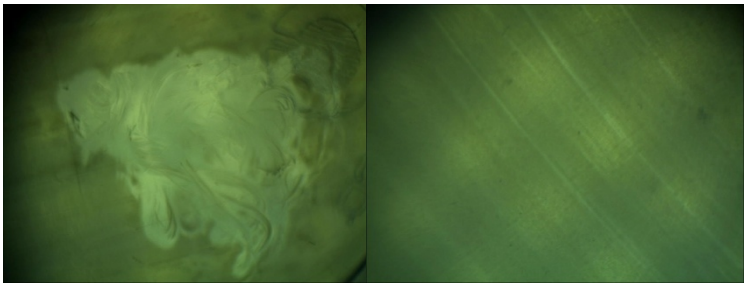

Fig7.Inhibitory effect of grafted PET fibers against E.coli

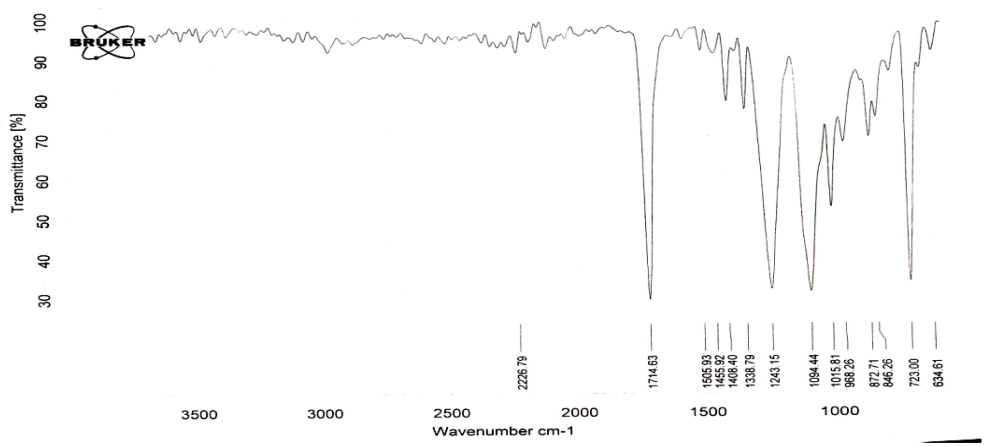

Fig 8.FTIR spectrum of ungrafted PET fiber

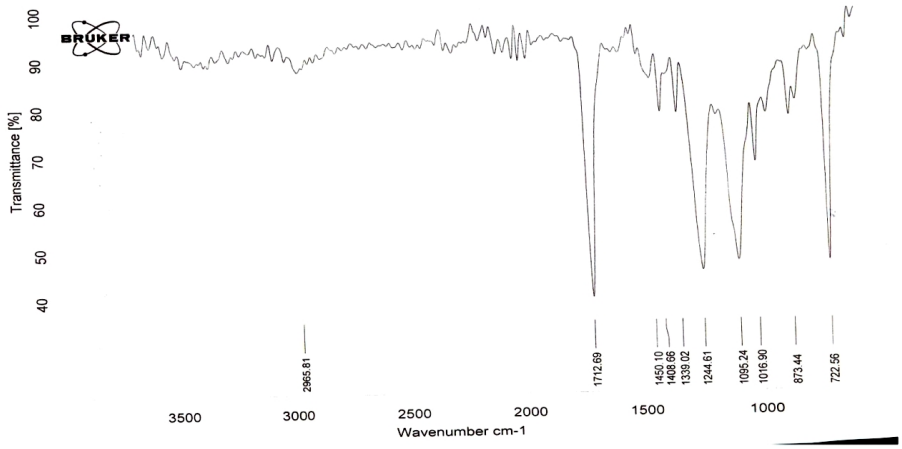

Fig9. FTIR spectrum of 2-HPMA/AAm grafted PET fiber

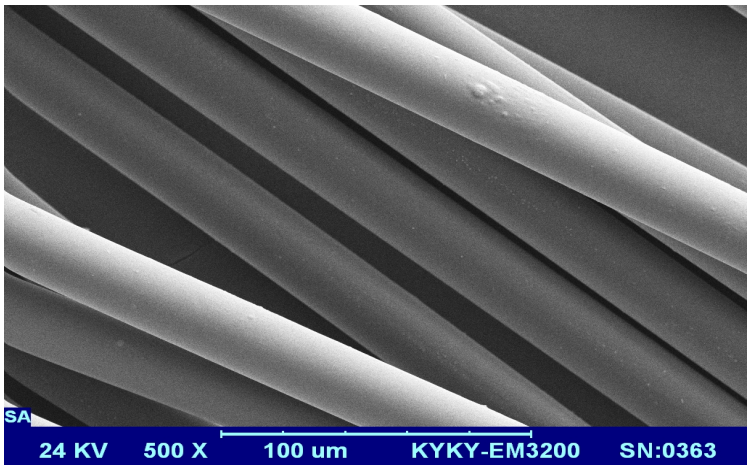

Fig10. SEM micrograph of ungrafted PET fiber

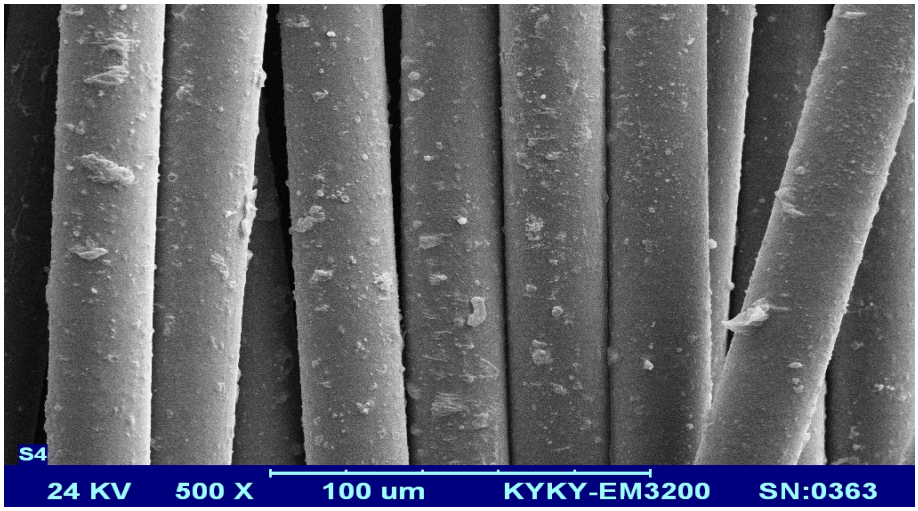

Fig11. SEM micrograph of AAm/2-HPMA mixture (46.0% grafted) onto PET

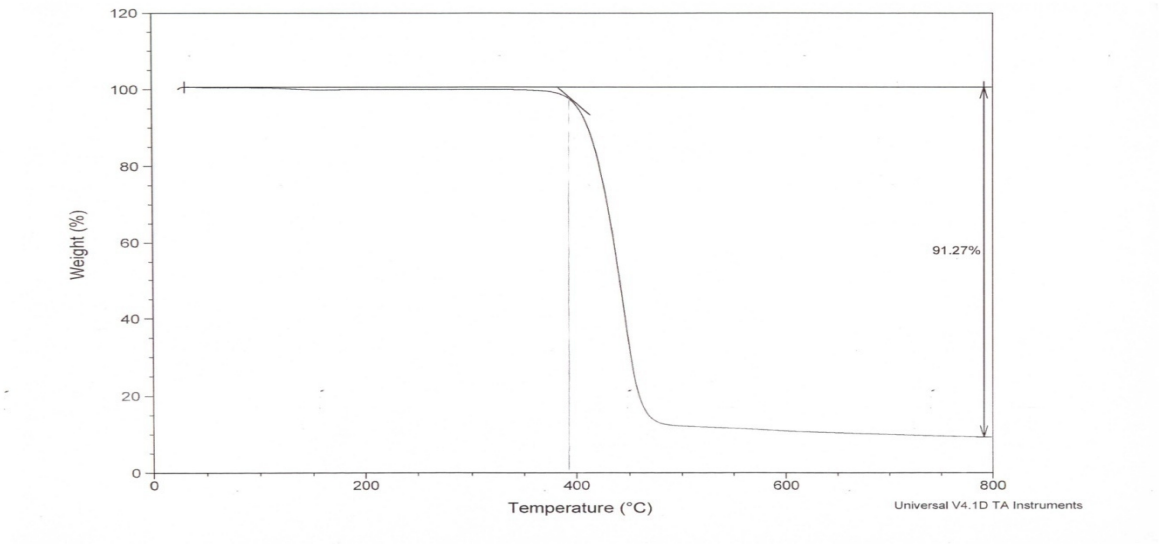

Fig12. Thermogram of ungrafted PET fiber

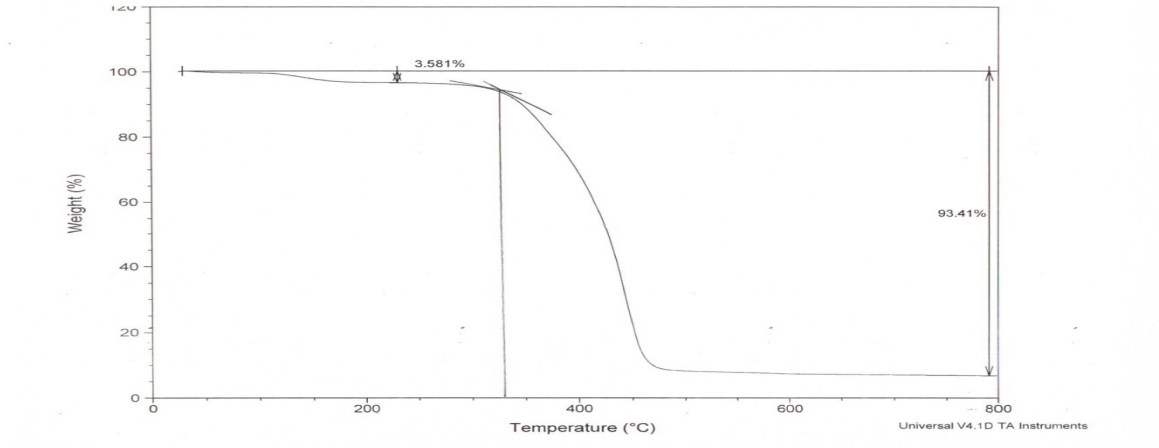

Fig13. Thermogram of AAm/2-HPMA mixture (46.0% grafted) onto PET

Table1. The variations of diameter and moisture regain with the percentage of grafting

Grafting yield (%)	Diameter ($mm \times 10^{-2}$)	Moisture regain (%)
0.0	1.44	0.42
11.2	1.67	0.86
20.6	1.86	1.43
46.0	2.12	2.18

Table2. Mechanical properties of the fibers

Grafting yield (%)	Tensile strain (%)	Tenacity (gf/tex)
0.0	73.13	40.12
11.2	62.08	38.42
16.8	59.37	32.83
46.0	42.71	29.90

Table3.Dependence of the rate of grafting on monomer mixture concentration ([Bz_2O_2] =4.0×10^{-3}mol/dm^3, t=15min, T=263K)

[AAm/2-HPMA] (mol/dm^3)	G (%)	R_g×10^4 (mol/dm^3.S)	Log[AAm/2-HPMA]+3	logR_g+4
0.05	12.50	10.38	1.699	1.016
0.10	17.30	14.44	2.000	1.159
0.15	22.00	18.33	2.176	1.263
0.20	28.00	23.33	2.301	1.368

Table4.Dependence of the rate of grafting on initiator concentration ([AAm/2-HPMA] (AAm20%+2-HPMA80%)=0.2 mol/dm^3,t=15min,T=263K)

[Bz_2O_2]×10^3(mol/dm^3)	G (%)	R_g×10^4 (mol/dm^3.S)	Log[Bz_2O_2]+4	logR_g+4
1	11.75	9.777	1.000	0.990
2	16.70	1.388	1.301	1.142
3	21.50	1.788	1.477	1.252
4	28.00	2.333	1.602	1.368

Table5.Values of the rate of grafting at different temperatures ([Bz_2O_2] = 4.0×10^{-3} mol/dm^3,[AAm/2-HPMA](AAm 20%+2-HPMA 80%) = 0.2 mol/dm^3,t=60min

T(K)	G (%)	R_g×10^4 (mol/dm^3.S)	1/T×10^3	logR_g+4
368	21.30	4.444	2.958	0.647
348	33.60	6.944	2.873	0.841
358	34.50	7.083	2.793	0.850
363	46.50	9.722	2.754	0.987

CONCLUSION

The experimental results showed that, the using of the monomers concurrently causes a synergistic effect on the grafting yield. Optimum condition for grafting were determined to be [Bz_2O_2] = 4.0×10^{-3} mol / dm^3, [AAm / 2-HPMA] (20% AAm+ 80% 2-HPMA) = 0.2 mol / dm^3, temperature = 90̊ C, time = 60 min. It was identified that, with an increase in the grafting yield, moisture regain and diameter increased. The rate of grafting was found to 0.57 powers of monomers and 0.61 of initiator, respectively. Therefore, the total degree of grafting is 1.18.The overall activation energy for grafting was calculated as 27.84 kJ/mol. However, the mechanical properties of the fibers decreased, but their levels are still acceptable

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