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European Journal of Experimental Biology, 2014, 4(1):560-567

ISSN: 2248 –9215
CODEN (USA): EJEBAU

Free radical grafting of 2-hydroxypropyl methacrylate/acrylic acid mixture onto poly (ethylene terephthalate) fibers

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ABSTRACT

I*n this study the chemical grafting of 2-hydroxypropyl methacrylate / acrylic acid (2-HPMA/AA) mixture onto poly (ethylene terephthalate) fibers using benzoyl peroxide (Bz_2O_2) as a radicalic initiator in aqueous media was investigated. The use of 2-HPMA as a comonomer increased the amount of AA introduced to the PET fibers up to 42%, while the grafting of AA fibers alone gave low graft yields. Optimum condition of grafting was determined to be [Bz_2O_2] = 4.0×10^{-3}mol/dm^3, [monomer mixture] (20% AA+80% 2-HPMA) = 0.2mol/dm^3, temperature = 90C and time = 60min. With an increase in the grafting yield, moisture regain and dye ability with acidic and basic dyes increased. The grafted fibers were characterized by thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR).*

Keywords: Poly (ethylene terephthalate), graft copolymer, 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. [1-11] 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 AA [2,3,7] and 2-HPMA[5,6] individually onto PET was reported, but using a binary mixture of (2-HPMA/AA) is not available in the literature. This article reports the grafting of 2-HPMA/AA 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.

MATERIALS AND METHODS

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 50C. 2-HPMA and AA were purchased by Merck (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 supplied by Merck and doubly distilled water was used in all experiments. The basic (Cationic Brill Red X-5GN) and acidic (Erionyl Yellow) dyes were purchased from Institute for Color and Technology (ICST) Iran.

Grafting procedure

Grafting was carried out in a 100 mL pyrex tube. The polymerization tube containing the PET fiber specimen (0.15±0.01g) , appropriate amount of the monomer mixture and 18 mL doubly distilled water was placed in water bath(Lauda D40S , Germany) , and kept there for 2 minute. Then 2 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 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 50C. 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.

Dying procedure

The fiber samples (grafted and ungrafted) were dyed with 1.5 g/dm^3 Erionyl Yellow A 36-01(acidic dye) and 2.0 g/dm^3 Cationic Brill Red X-5GN (basic dye) at 90C for 120 min in water bath. Dye ability was determined by the use of Shimadzu UV-1601-PC spectrophotometer at λ_{max}(346nm) and (513.5nm) , respectively.

Determination of moisture regain and diameter

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

2) $\text{Moisture regain}\ (\%) = (M_n - M_0) / M_0 \times 100$

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×.

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 25-800C at a heating rate of 10C.

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 AA and 2-HPMA. As shown in **Fig.1**, when AA 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 (42%) at a (20%AA+80%2-HPMA). [13-18]

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 [6, 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. [10, 11]

Characterization of the fibers

The results obtain from FTIR spectrum of grafted PET fibers showed some changing as regards to ungrafted PET. Respectively, the adsorption bands at 2967 and 3470 cm^{-1} are related to alcoholic –OH group of 2-HPMA and acidic –OH group of AA. These new peaks confirm that, the PET fibers were grafted by both of monomers. [3, 6, 15] **Figs.4, 5**

As shown in **Figs .6, 7**, with an increase in grafting yield, the fibers structure showed a heterogeneous structure and their surfaces observed so rough. [6, 11, 13] data showed that, the decomposition temperature of the fibers decreased after modifying. The thermal decomposition temperature of raw PET (395C) was decreased to (350C) at 42.0% grafted yield. **Figs .8, 9**

These results confirm that, the grafting of monomer mixture onto PET backbone. [3, 6, 14, 15]

Moisture regain and diameter

With an increase in the grafting yield, the water absorption capacity increased and at 42% of grafted fiber, it reached to 2.25%. This is attributed to the hydrophilic groups of –OH and –COOH in 2-HPMA and AA structures which grafted to PET backbone.[10,11,13,14]

The diameter of PET fibers showed an increasing from 1.44×10^{-2} mm (ungrafted fiber) to 2.43×10^{-2} mm (grafting percentage 42%)

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

Dye ability

Dye ability of the grafted fibers with Erionyl Yellow A36-01 and Cationic Brill Red X-5GN showed an increasing as regards to ungrafted fibers. Dye ability of the grafted PET fibers with acidic and basic dyes increased to 3.15 and 2.35 mg (dye)/g (fiber) at the 42% of the grafting yield (20%AA+80%2-HPMA), respectively. These values emphasize that the interaction of the –OH group of 2-HPMA with acidic dye and –COOH group of AA with basic dye. Results presented in **Table.1**

Mechanical properties of fibers

Instron vibromat set was used for determination of the mechanical properties, such as tensile strain, modulus 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]

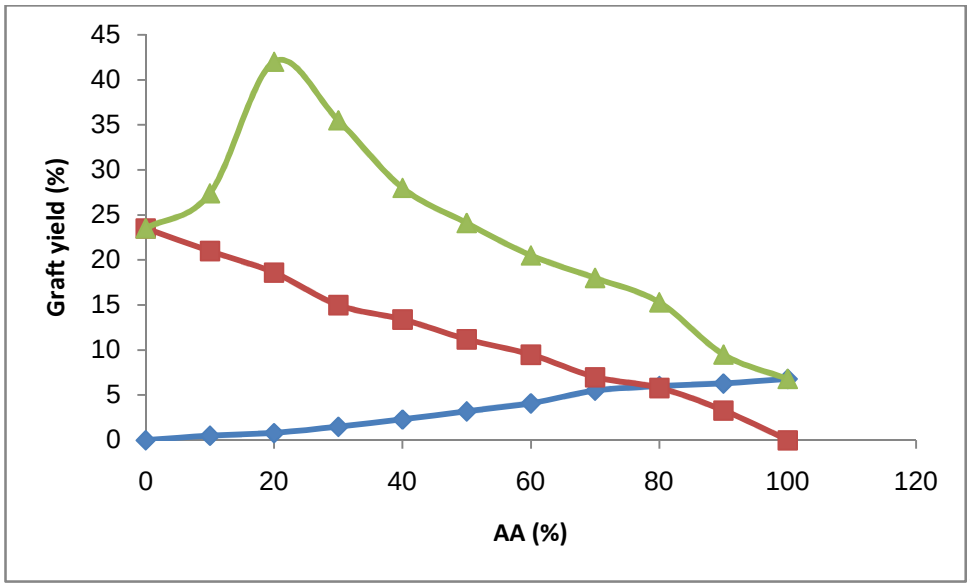

Fig 1.The grafting yields of AA, 2-HPMA and AA/2-HPMA mixture ([AA/2-HPMA]=0.2mol/dm^3 , Time=2h , Temperature=90C , [Bz_2O_2]=4.0×10^{-3}mol/dm^3)

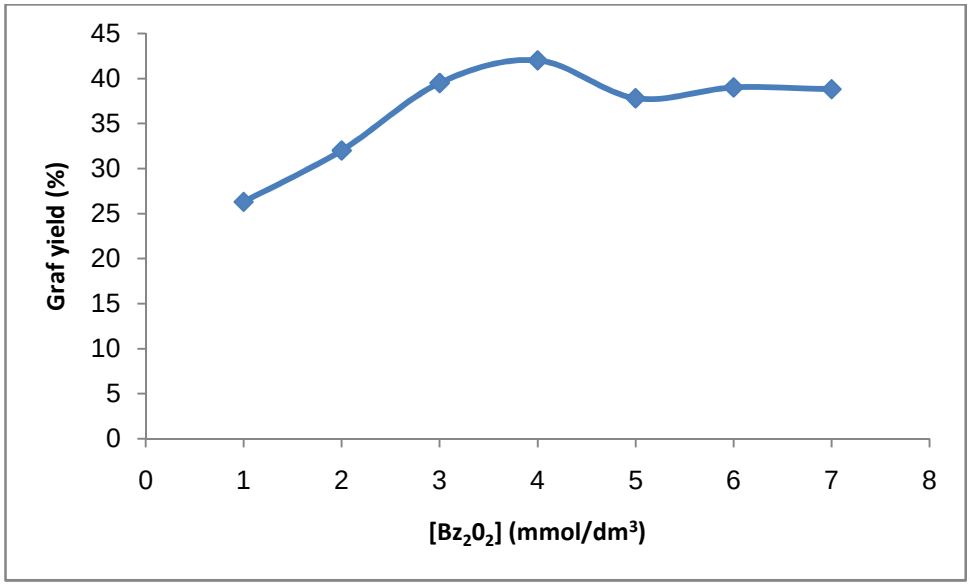

Fig2. Effect of Bz_2O_2 concentration on the grafting yield ([AA/2-HPMA] (20 wt% AA) = 0.2mol/dm^3 , Time=2h , Temperature=90℃)

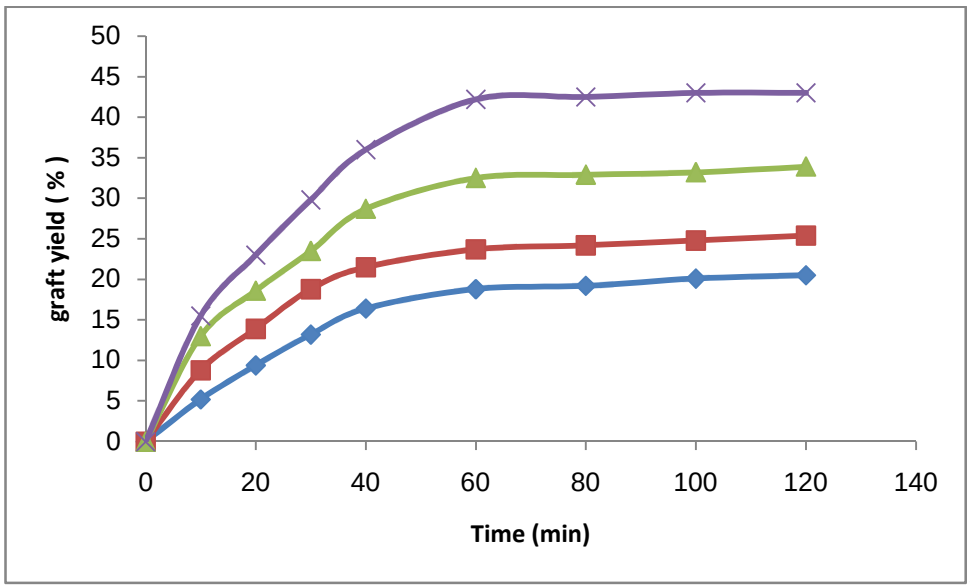

Fig3. Effect of temperature and time on grafting (◆) 65℃ , (■) 75℃ , (▲) 85℃ , (×) 90℃
([AA/2-HPMA] (20 wt% AA) =0.2mol/dm^3 , Time = 2h , Temperature = 90℃ , [Bz_2O_2] = 4.0×10^{-3}mol/dm^3)

Table 1. The variations of diameter, moisture regain and dye ability with the percentage of grafting

Grafting yield (%)	Diameter (mm×10^{-2})	Moisture regain (%)	mg(acidic dye)/ g(fiber)	mg(basic dye)/ g (fiber)
0.0	1.44	0.42	0.28	0.24
15.3	1.75	1.17	1.26	0.96
28.0	2.12	1.86	2.39	1.68
42.0	2.43	2.25	3.15	2.35

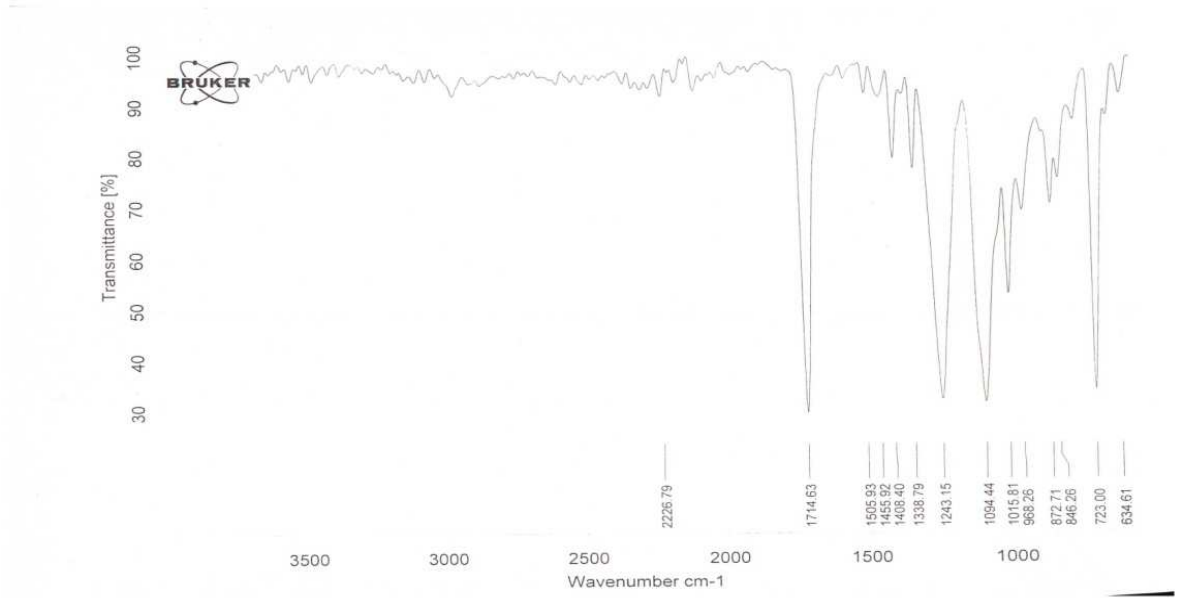

Fig 4.FTIR spectrum of ungrafted PET fiber

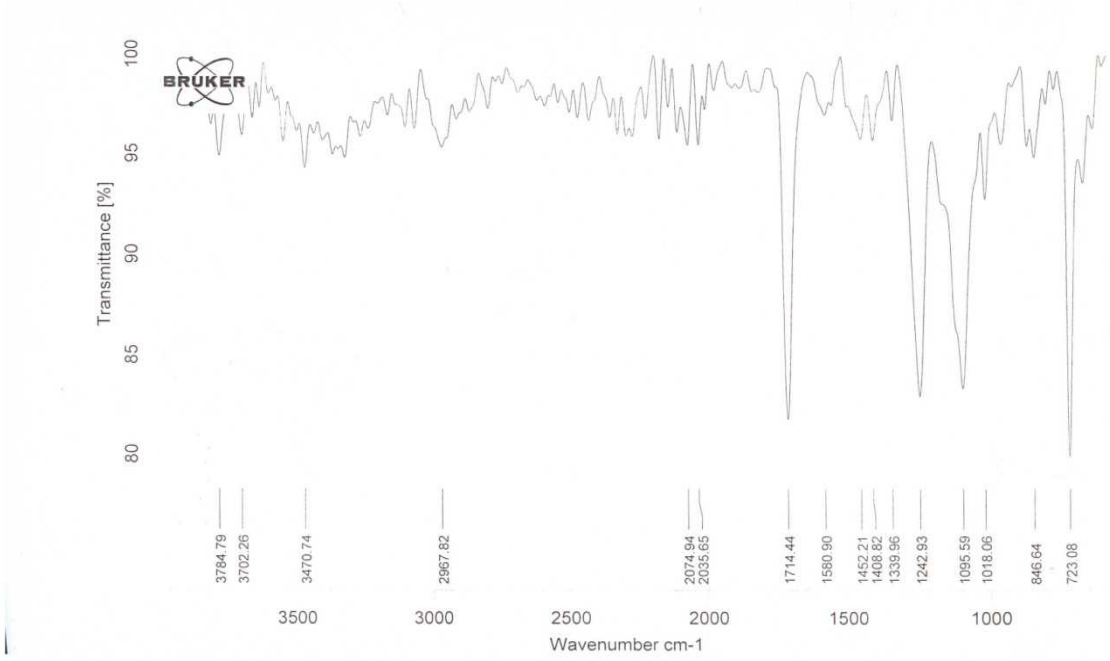

Fig5. FTIR spectrum of 2-HPMA/AA grafted PET fiber

Table 2. Mechanical properties of the fibers

Grafting yield (%)	Tensile strain (%)	Modulus (gf/tex)	Tenacity (gf/tex)
0.0	73.13	-13.75	40.12
9.5	70.83	-3.87	38.99
15.3	70.63	-3.63	35.84
42.0	61.46	-2.87	33.60

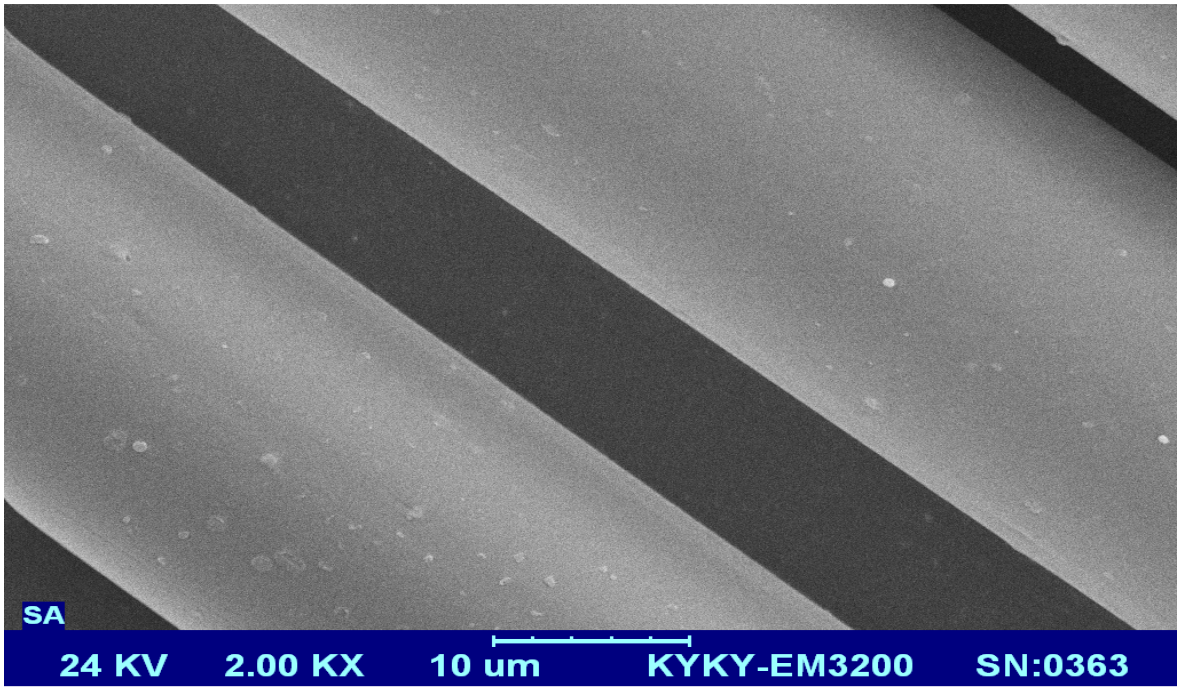

Fig6. SEM micrograph of ungrafted PET fiber

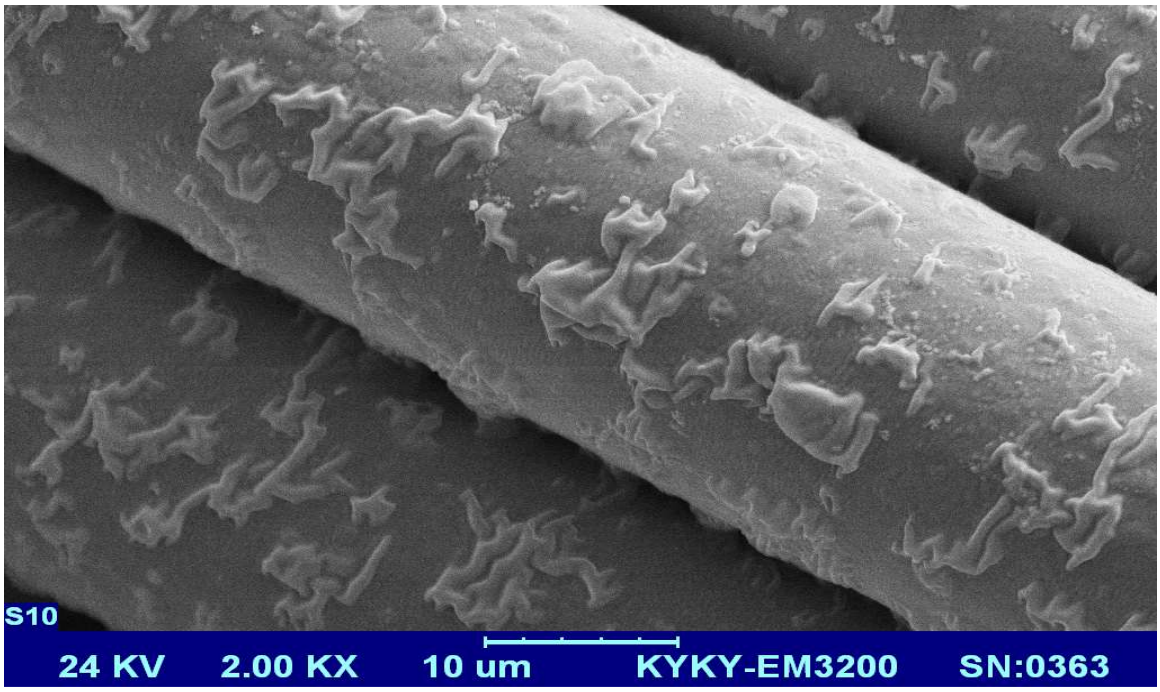

Fig7. SEM micrograph of AA/2-HPMA mixture (42% grafted) onto PET

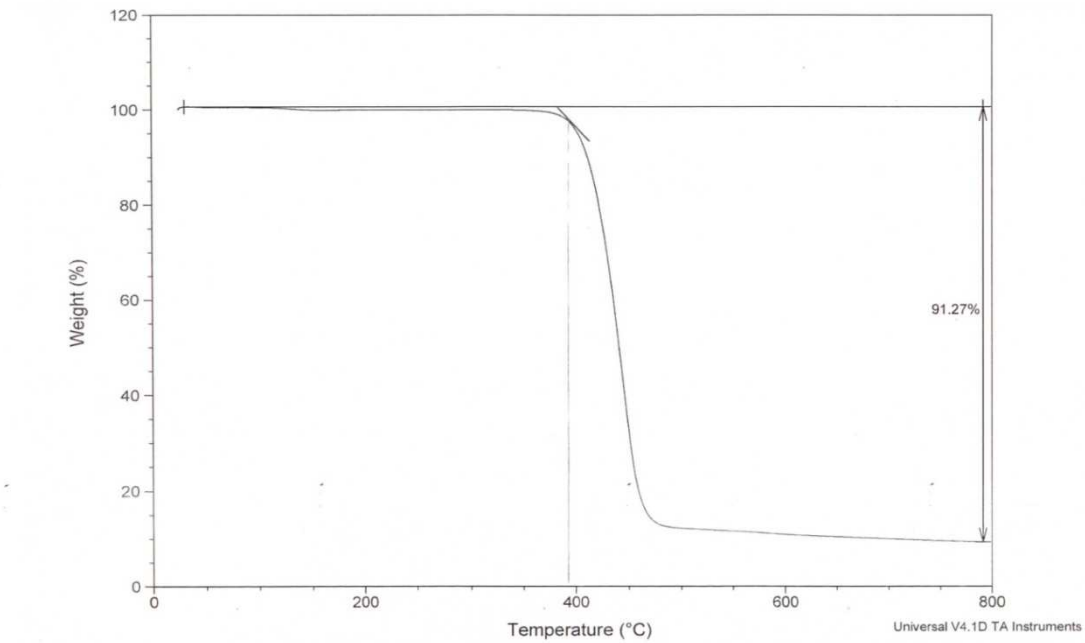

Fig8. Thermogram of ungrafted PET fiber

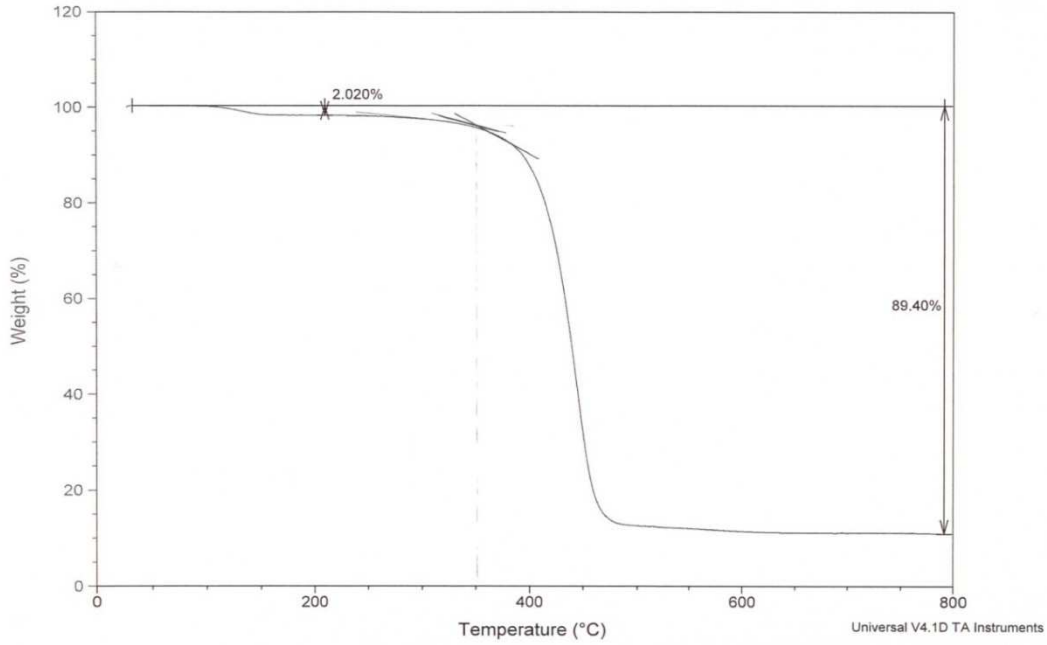

Fig9. Thermogram of AA/2-HPMA mixture (42% grafted) onto PET

CONCLUSION

The experimental results showed that, using of the monomers concurrently causes a synergistic effect on the grafting yield. Optimum condition for grafting were recorded to be $[Bz_2O_2]$ = 4.0×10^{-3} mol / dm^3, [AA / 2-HPMA] (20% AA+ 80% 2-HPMA) = 0.2 mol / dm^3, temperature = 90° C, time = 60 min. It was identified that, with an increase in the grafting yield, moisture regain, diameter and dye ability with acidic and basic dyes increased. However, the mechanical properties of the fibers decreased, but their levels are still acceptable.

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