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Functional modification of poly(ethylene terephthalate) with an allyl monomer: Chemistry and structure characterization

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ABSTRACT

Radical grafting of biocidal precursor monomer 3-allyl-5,5-dimethylhydantoin (ADMH) onto poly(ethylene terephthalate) (PET) fabric was investigated. Based on SEM pictures, it was suggested that benzoyl peroxide could generate macromolecular radicals on PET when it was delivered to the areas properly. The macroradicals were in a form of benzoyl structure which can react with ADMH to form a short chain graft. It seems the reaction occurred at the end of polymers or defect areas with terephthalate groups at the end. After being converted to *N*-chloramide structure, the poly(ADMH)-*g*-PET fabric demonstrates total kill of 10^5–10^6 CFU/mL *Escherichia coli* at a contact time of 2 h.

1. Introduction

Surface modification of poly(ethylene terephthalate) (PET) can introduce new functions such as biocompatibility, hydrophilicity, dyeability, adhesion, anti-fogging, anti-fouling, and antibacterial properties to hydrophobic materials [1–6]. Radical graft polymerization offers the most powerful and possibly the only means for the surface chemical modifications of chemically inert polymers. Plasma or γ ray initiation methods are effective ways to generate radicals on the polyester. Successful generation of macromolecular radicals on PET substrate could be evidenced by electron spin resonance spectra, but without solid evidence of reactions between PET and some functional monomers [7,8]. Since 1970s, many researchers have used radical graft polymerization to incorporate different functional monomers to PET [9–14]. However, Wilkie claimed that in most graft polymerization reactions a semi-interpenetrating network rather than chemically grafting was formed in grafting methacrylic acid (MAA), methyl methacrylate, styrene or vinyl alcohol onto polyesters when one of the following compounds such as hydrogen peroxide, benzoyl peroxide, azobisisobutyronitrile, and cobalt acetylacetonate was used as an initiator [15].

As a goal of preparing durable and regenerable antibacterial polyester fibers, surface grafting of a halamine precursor monomer, 3-allyl-5,5-dimethylhydantoin (ADMH), onto polyester fibers was planned. Solvents with solubility parameter close to polyesters were chosen to deliver functional monomer and initiator for optimal contact between the surfaces and the chemicals. The graft polymerization was initiated in solid state status after the initiator and monomer were efficiently delivered to surfaces of the fibers. To confirm the chemical grafting, the treated polyester fabrics were hydrolyzed, and the hydrolyzed mixtures were analyzed by infrared and mass spectroscopies.

2. Experimental

2.1. Materials and reagents

Polyester plain woven fabric (PET, #755H), purchased from Testfabrics, Inc. (West Pittiston, PA). Benzoyl peroxide (BPO, Acros, Pittsburg, PA) and potassium persulfate (PPS, Acros) were recrystallized from solvent systems of chloroform/methanol, and distilled water, respectively. 3-Allyl-5,5-dimethylhydantoin (ADMH) was synthesized according to a method reported previously [16].

2.2. Radical grafting polymerization

All chemicals (monomer and initiator) were dissolved in methanol at certain ratios, and PET fabric swatch was soaked in the above solution for 24 h. The solution was then air-dried on the fabric to get approximately 40% dry add-on (based on the weight of fabric). The fabric was cured in an oven for a certain period of time. After the grafting polymerization, the PET sample was

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Soxhlet-extracted with acetone for 24 h, dried at 105 °C, and stored in a desiccator for 48 h to reach constant weight.

Percentage graft was calculated from the following equation:

$$\%\ \text{Grafting} = (W2 - W1)/W1 \times 100$$

where $W1$ and $W2$ are the weights of the pristine and the grafted PET, respectively.

The grafted samples used for mechanistic study, instead of being extracted with acetone, were only washed with large amounts of DI water. So, trace amount of unreacted ADMH can be kept to serve as internal standard in the following Mass spectrometry analysis.

2.3. FTIR analysis

FTIR spectra were taken on a Nicolet 6700 spectrometer (Thermo Electron Corporation) using KBr pellets.

2.4. Mass spectrometry analysis

To characterize the chemically modified PET structures, alkaline hydrolysis method was used to break the polymer to ethylene glycol and sodium terephthalate. The modified PET was hydrolyzed at 100 °C in a 11.87% KOH solution, and then neutralized by a 7.6% HCl solution, the amount of which is 1.05 times the KOH by weight. After hydrolysis, the so-formed disodium terephthalate and its derivatives (if grafted) could be separated by acidification (using 7.6% HCl solution) to obtain solid terephthalic acid (TPA) and its derivatives, while ethylene glycol (EG) and its derivatives can be recovered by dichloromethane extraction.

Recovered terephthalic acid (TPA) and its derivatives were then re-dissolved in KOH solution (50% methanol) for MS analysis (named as "TPA Portion"). Dichloromethane extracts were dissolved in 50% methanol doped with 0.1% formic acid after removing dichloromethane under vacuum (named as "Soluble Portion"). The extraction was analyzed by using a mass spectrometer (ESI/MS) (AB MDS SciEX Q TRAP) to find its contents. The spectrum was acquired by syringe infusion of the analyte at 15 μL/min into the ESI source. A good quality spectrum was obtained by averaging the acquired data over a period of 1 min. In Collision Induced Dissociation (CID) experiments on the mass spectrometer, nitrogen was used as the collision gas, and normalized collision energy of 35% was used to bring about fragmentation.

2.5. Electron microprobe and scanning electron microscope

High resolution sulfur elemental mapping and high speed backscattered electron (BSE) imaging were taken with Cameca SX-100 electron microprobe (CAMECA Instruments Inc., USA). Surface morphology of grafted PET fabric was observed using Philips XL30 Scanning Electron Microscope (SEM).

2.6. Chlorination

The PET samples (PADMH grafted) were converted to halamine structure in a simple chlorination process. The samples were immersed in a diluted chlorine bleach solution (containing 3000 ppm available chlorine) at room temperature for 30 min. The liquid to fabric (liquor) ratio was 50:1 (w/w). The fabrics were then rinsed in copious amounts of distilled water and air dried. An iodometric titration method was adopted in quantification of the active chlorine content on the samples. 0.5 g ± 0.001 of sample fabric was cut into small pieces and then added into 15 mL of 0.001 N sodium thiosulfate standard solution. After 30 min shaking, the excess amount of sodium thiosulfate in the mixture was titrated with 0.001 N iodine standard solution by monitoring mV changes with a redox electrode (platinum Ag/AgCl). The active chlorine of the grafted samples was then calculated from the following equation:

$$\text{Active chlorine (ppm)} = 35.45 \times (V1 - V2) \times N \times 1000/2 \times W$$

where V_1 and V_2 are the volumes (mL) of the iodine solution consumed in titrations of blank sodium thiosulfate solution and that with PET sample in, respectively, N is the normality of iodine solution and W is the weight of the samples in grams.

2.7. Antibacterial assessment

Antibacterial properties of the grafted samples were examined according to a modified American Association of Textile Chemist and Colorists (AATCC) test method 100 against a nonpathogenic Gram-negative bacterium *Escherichia coli* K-12 (*E. coli*, UC Davis Microbiology Laboratory). The fabrics were cut into four small pieces (ca. 4 cm^2). Two pieces of the samples were put together in a sterilized container and 1.0 mL of an aqueous suspension containing 10^5–10^6 colony forming units (CFU)/mL of *E. coli* was placed onto the surfaces of the fabrics. The fabrics were then "sandwiched" using another set of two identical fabrics. To ensure sufficient contact, a sterilized 50-mL beaker was placed onto the top of the fabrics. After different contact times, the entire "sandwich" was placed into 100 mL of 0.03% sodium thiosulfate aqueous solution to quench the active chlorine on the fabrics. The resultant solution was then vigorously shaken for 5 min. An aliquot of the solution was removed from the mixture and then serially diluted and 100 μL of each dilution were placed onto a nutrient agar plate. The same procedure was also applied to the bleached ungrafted and the grafted but unbleached PET fabrics as controls. Viable bacterial colonies on the agar plates were counted after incubation at 37 °C for 24 h. Bacterial reduction is reported according to the following equation.

$$\text{Percentage reduction of bacteria}\ (\%) = (A - B)/A \times 100$$

where A is the number of bacteria counted from control fabrics, and B is the number of bacteria counted from grafted and bleached fabrics.

3. Results and discussion

3.1. Graft polymerization on PET

Radical graft polymerization method is one of the most widely used methods that can chemically modify surfaces of polyester fibers. The reaction involves the following steps:

$$I_2 \rightarrow 2I^{\bullet} \quad (1)$$

$$2I^{\bullet} + \text{PET—H} \rightarrow \text{PET}^{\bullet} + \text{I—H} \quad (2)$$

$$\text{PET}^{\bullet} + \text{M} \rightarrow \text{PET—M} \quad (3)$$

$$I^{\bullet} + \text{M} \rightarrow \text{I—M} \quad (4)$$

where $I^{\bullet}$ is a primary radical generated from the initiator, PET–H is the polyester backbone and M is the functional monomer. The reaction (2) is a hydrogen abstraction reaction on polyester. $PET^{\bullet}$ represents a macroradical formed on polyester. $I^{\bullet}$ can undergo

addition reaction with the monomer (Equation (4)) or hydrogen abstraction (Equation (2)). A number of studies have found that increasing nucleophilicity of the attacking radical favors abstraction over addition to an unsaturated system (benzene ring or double bond) [17–19]. Most radical initiators generated from dissociation of peroxides favor hydrogen abstraction reaction and are employed in graft polymerization reactions [17]. Benzoyl peroxide (BPO) was selected because it is a peroxide initiator and has strong affinity towards PET backbone. Besides, if the graft reaction temperature was set at 120 °C, at which the half degradation time ($t_{1/2}$) of benzoyl peroxide (BPO) is 3 min, 97% decomposition of the initiator can be ensured in 15 min. Such a temperature–time frame is most suitable for chemical finishing processes on polyester fibers.

3.2. Generation of macromolecular radical on PET fabric with BPO

In a previous work on graft polymerization on cellulose [20], a hydrophilic initiator, potassium persulfate (PPS) was proven as an effective radical generator on the polymer. In that case sulfur elements were observed by element mapping technology and served as an evidence of successful generation of cellulosic radicals. PPS is not a suitable radical initiator on PET since they do not have any affinity with each other. But, if macroradicals are generated on the polymer, additional PPS radicals may react with the macroradicals to form sulfur containing surfaces on PET, which can be directly observed from sulfur element mapping experiment. So, both initiators, benzoyl peroxide (BPO) and PPS, were used in the study, while BPO is a potential radical initiator on polyesters.

Generally speaking, ideal initiators should have great affinity to and be able to penetrate through surfaces of the polymer. Use of a swelling agent could facilitate the grafting reactions onto PET [21–23], which was also considered in this study. PET may be considered as an $(AB)x$ alternating copolymer, where A is the aromatic segment $–CO–C_6H_4–$ having a solubility parameter (δ) value of 9.8 and B is an aliphatic ester $–CO–O–CH_2–CH_2–$ having a δ value of 12.1 [24]. So the solvents with δ close to those of PET (δ: 9.8 and 12.1) were chosen for reagent delivering purpose: acetone (δ: 9.77), dimethyl sulfoxide (δ: 13.0), and methanol (δ: 14.28).

Following the spray of acetone solution of BPO onto the PET fabric and air-drying, dimethyl sulfoxide solution of PPS was put onto the substrate. Afterwards, the sample was cured at 120 °C for 20 min. After the completion of the reaction, the PET fabric was extracted with acetone in a Sohxlet extractor for 24 h. Finally, the PET sample was submitted for electron microprobe analysis. Unfortunately, there was no obvious increase of sulfur signal after the treatment (Fig. 1), indicating that the primary sulfate radical was not fixed on the PET substrate. However, the oxygen mapping test revealed that the oxygen content increased dramatically on the treated PET fabric, which could be a result of the reaction between oxygen in air and the macroradicals on PET. This is a strong indication of generation of polyester macroradicals by BPO. The failure of sulfate primary radicals reacting with macromolecular radicals could be caused by low affinity between PPS and the polymers.

In a separate test, only BPO was loaded onto PET fabric in acetone following the same procedure. The molar ratio BPO to PET repeating unit was changed in the range of 0.0725–0.65. At the highest BPO loading (molar ratio of BPO to PET repeating unit equals 0.65), surface morphologic changes of the fabrics were observed, shown in Fig. 2. It appears that the reactions occurred at the ends of the fibers or some defect areas. The enlarged SEM pictures show some

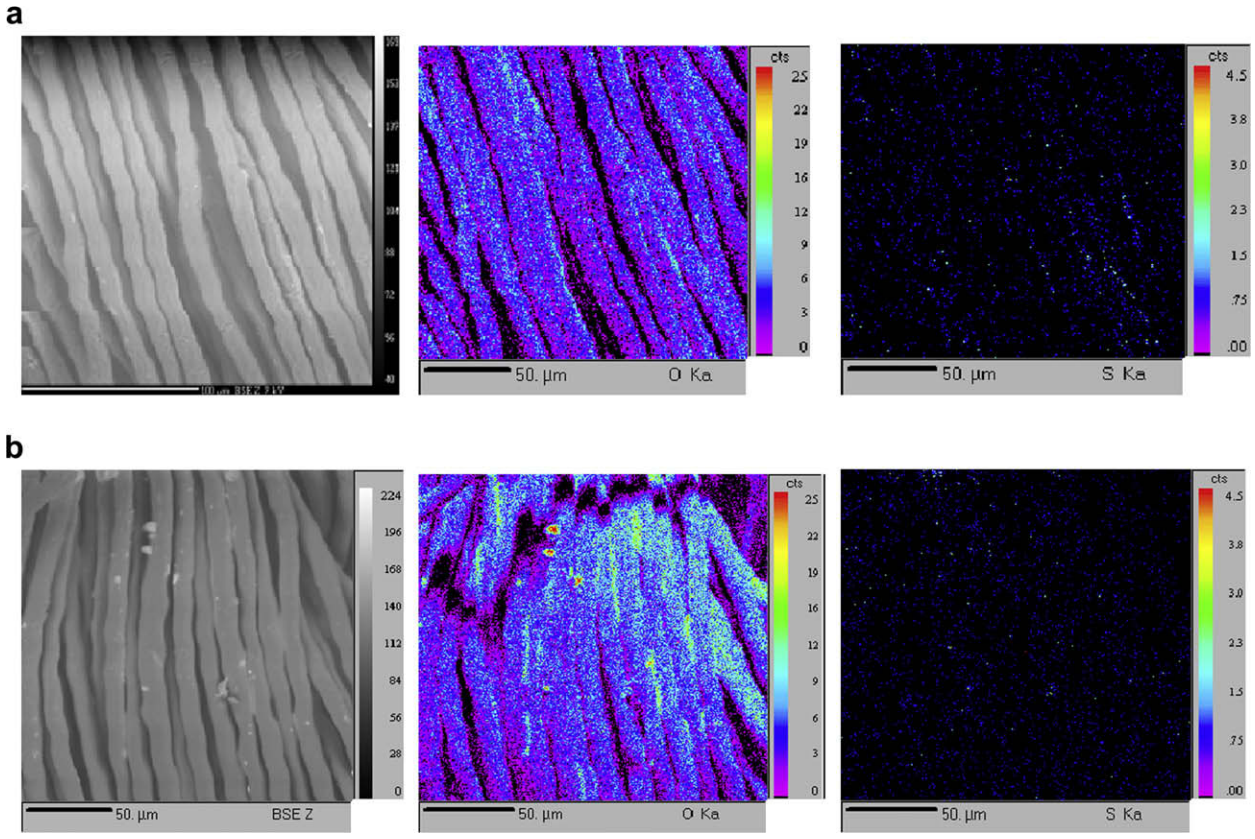


Fig. 1. Microprobe images (left pictures: backscattered; middle picture: oxygen mapping; right pictures: sulfur mapping) of (a) untreated PET fabric. (b) initiator treated PET fabric.

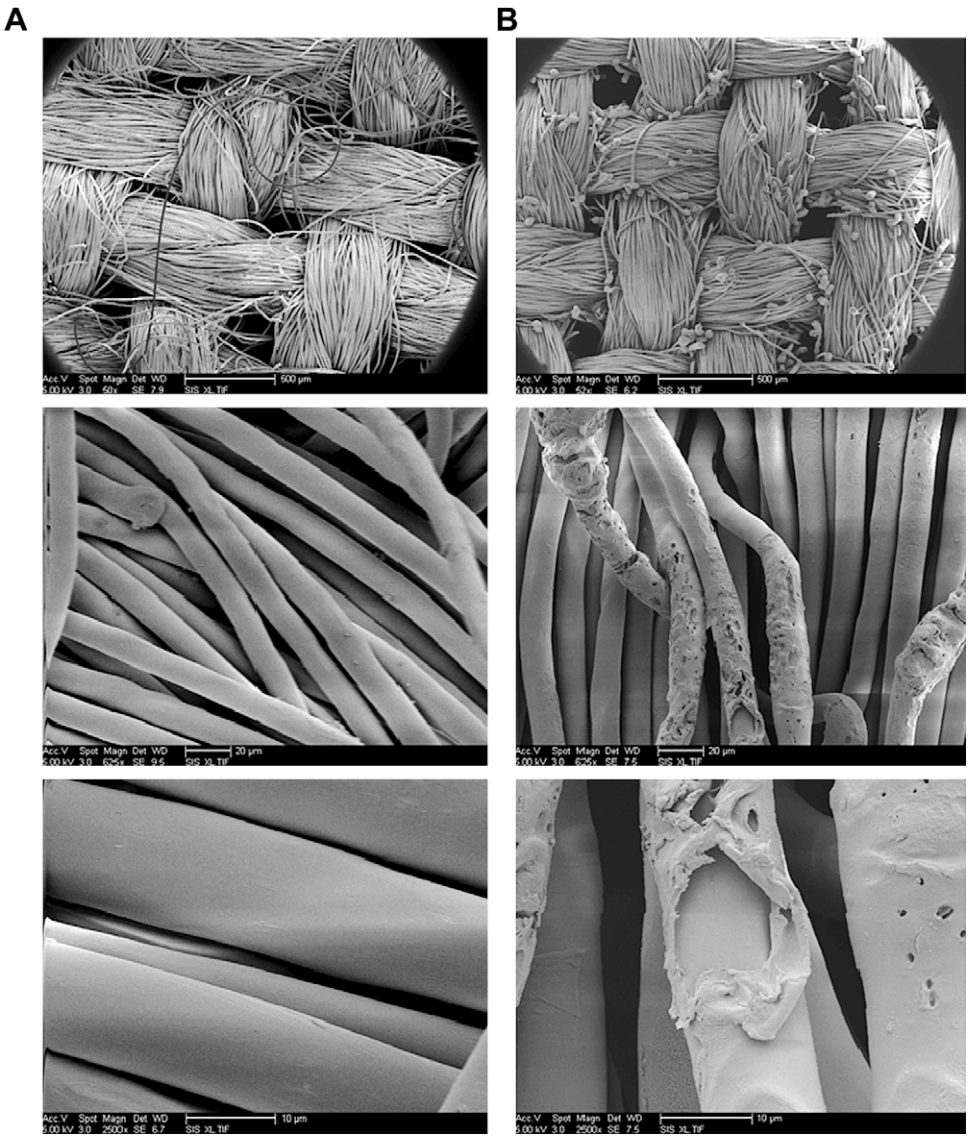


Fig. 2. Surface morphology of untreated (A) and treated (B) PET fabrics.

details at the damaged areas on fibers. Obviously, the initiator BPO reacted with the PET substrate, which is another evidence of the formation of macroradicals on the polymers.

3.3. Grafting mechanisms

Then, the graft polymerization was conducted by applying both BPO and 3-ally-5,5-dimethylhydantoin (ADMH) on the polyester fabrics. Methanol was employed as a solvent in this study since it is a good swelling agent for PET, and a solvent for both BPO and ADMH. An extreme condition was designed to maximize the graft polymerization on PET surfaces. A total of 10 g of PET fabric were soaked in 120 mL methanol containing 2.09 g BPO (8.65 mmol) and 2.91 g ADMH (17.3 mmol) for 24 h. Following such a long duration of soaking, the solution was dried on the surface of PET sample. Then, the sample with approximately 40% dry add-on was cured at 120 °C for 20 min and washed with large amounts of distilled water.

Normally, surface grafting reactions have low yields due to limited surface areas, which make it difficult to characterize the grafted structures on PET. Therefore, a depolymerization process was employed to characterize the product structures. Many scientists studied the depolymerization of PET for recycling purpose [25–29]. Ammonolysis, glycolysis and hydrolysis are all possible chemical depolymerization methods [30]. To reduce complexity of the whole system in analysis, only hydrolysis was considered. Although acidic hydrolysis is effective, removal of the formed terephthalic acid on the unreacted PET fibers requires usage of solvents such as DMSO. So, hydrolysis of grafted PET under alkaline condition was adopted, which is also preferred for retaining the grafted hydantoin structures.

A total of 10 g of the grafted PET fabric were immersed in a 250 mL round-bottomed flask with 100 g 11.87% KOH solution (mole ratio of PET repeating units to KOH = 1:4) and a magnetic stirring bar. The flask was then equipped with a condenser and placed in a heated oil bath set at 100 °C to initiate the hydrolysis. Reaction mixture 5 mL was taken out in a time interval of 20 min, and at the same time 5 mL fresh KOH solution was added. After hydrolysis, the so-formed disodium terephthalate and its derivatives (if grafted) could be separated by acidification (using slightly excess 7.6% HCl solution) to obtain solid terephthalic acid (TPA) and its derivatives, while ethylene glycol (EG) and other soluble

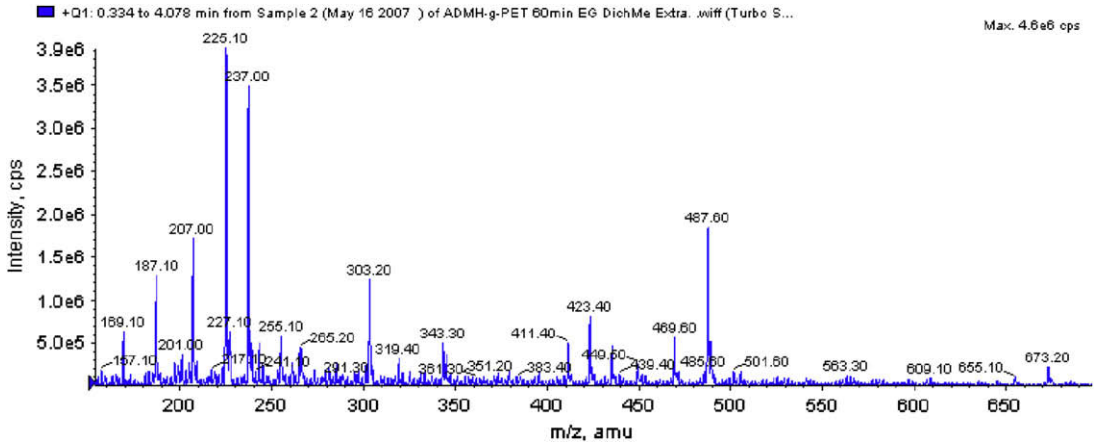


Fig. 3. Positive mass spectrum of the "Soluble Portion" of ADMH-*g*-PET (1 h hydrolysis).

derivatives can be recovered by dichloromethane extraction. The mass spectra were acquired by directly injecting the analytes into the electrospray source of the Applied Biology Quadrupole Mass Spectrometer.

In the positive mass spectrum of the "Soluble Portion" (Fig. 3), several ion peaks were found: *m*/*z* 169, 187, 225, 237, 303, 319, 469, 487, 655. The ion *m*/*z* 169 is the unreacted ADMH, CID spectrum of which (shown in Fig. 4) fits perfectly with that of pure ADMH. Based on the CID spectrum in Fig. 4, the ion *m*/*z* 187 was identified as 3-(3-hydroxyl propyl)-5,5-dimethylhydantoin, which was also found in the grafting of ADMH onto cotton cellulose [20]. Such a product should be a result of addition of hydroxide radical to ADMH. Since the reaction was conducted in ambient air the existence of oxygen gas may quickly react with macroradicals to form peroxide radicals and possibly hydroxyl radicals consequently, which could be the reason of strong oxygen mapping signals (Scheme 1). Phenyl radical is the β-scission product of benzoate radical.

The ions *m*/*z* 319, 487, 655 are ion series spaced by 168 (molecular weight of ADMH), which again indicates they are poly (ADMH) oligomers. The end group of those oligomers equals 319–169 = 150 fitting well with the molecular mass of terephthalaldehydic acid. The possible mechanisms are depicted in Scheme 2. The carboxylic acid bond undergoes a cleavage to form a substituted benzoyl radical (–PhC(O)•) (Scheme 1). In the presence of oxygen, that radical can react with oxygen to form substituted benzoyl hydroperoxide, resulting oxygen rich surfaces. The substituted benzoyl radical can then react with allyl group in ADMH to form grafted polymer, while the peroxide structure may undergo further decomposition to hydroxide radical and benzoate radical (Scheme 2). The addition of benzoyl radical to an alkene is not uncommon [31]. The smaller bond dissociation energy of C(O)–O (269 kJ/mol) compared with C–H (around 360 kJ/mol) also explains the C–O bond rupture instead of the hydrogen abstraction. The formation of 3-(3-hydroxyl propyl)-5,5-dimethylhydantoin (*m*/*z* 187) may be formed via two pathways: (1) hydroxyl radical adds onto the monomer; (2) benzoate radical adds onto the monomer, followed by depolymerization hydrolysis (Scheme 2). In CID, ions *m*/*z* 225, 237, 303

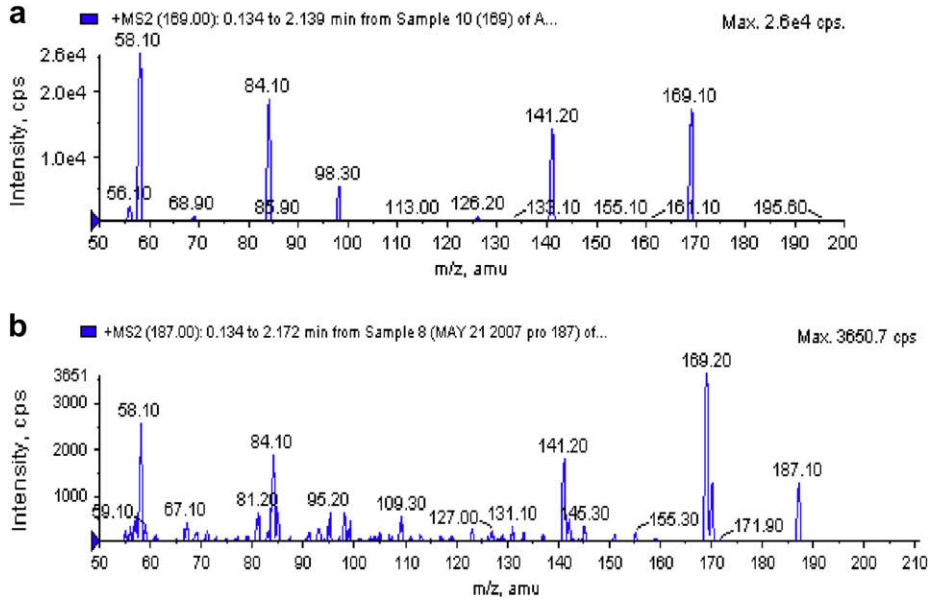
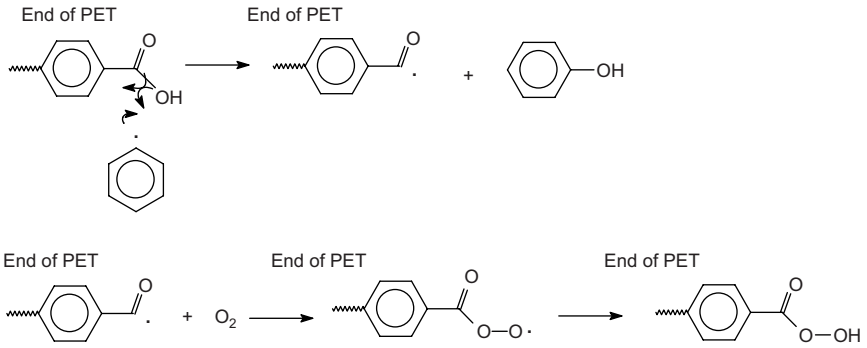


Fig. 4. Collision induced dissociation (CID) spectra of ions *m*/*z* 169 (a), 187 (b).



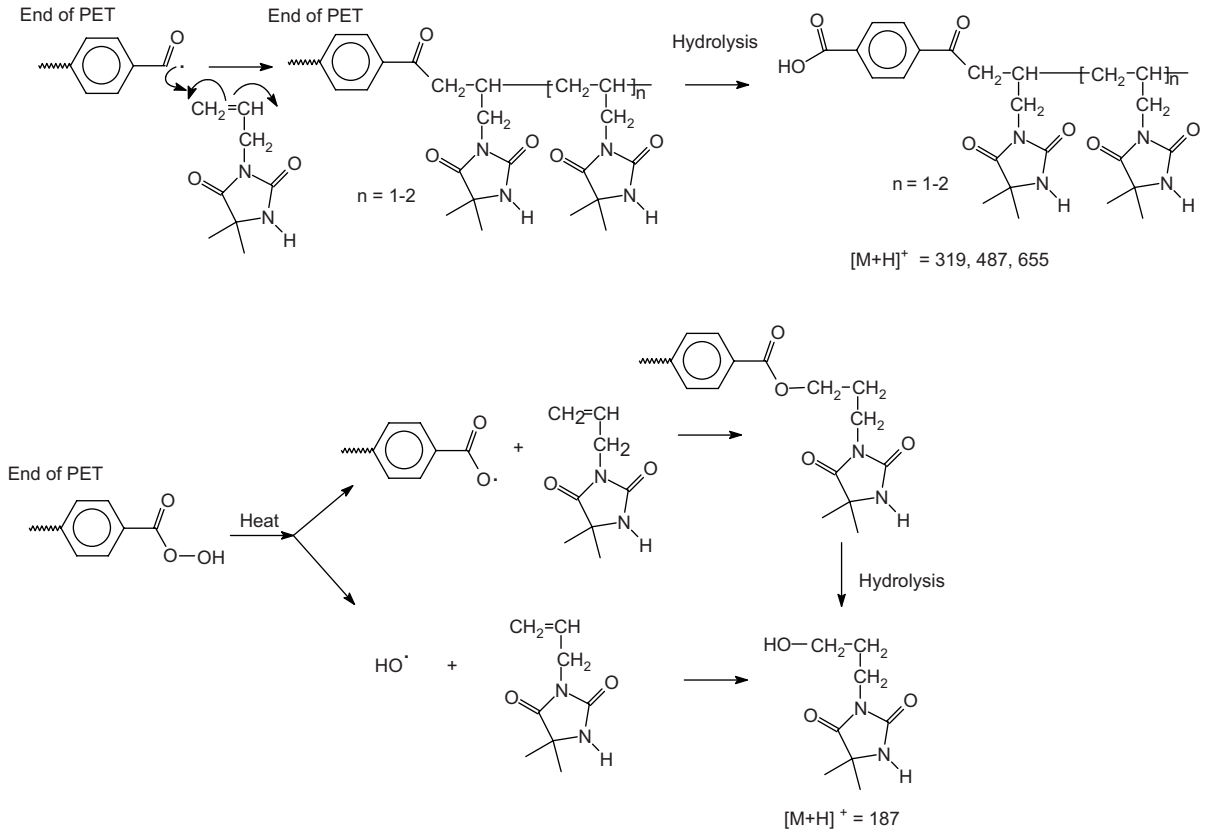
Scheme 1. Possible formation of radicals and oxygen rich surfaces on polyester fibers.

lose one water molecule and both ions *m*/*z* 225 and *m*/*z* 303 fragment to give ions *m*/*z* 142 and *m*/*z* 168. But it is hard to assign them at this point.

The IR spectrum of "Soluble Portion" further supports the hypothesis proposed above. As shown in Fig. 5, stretching peaks of the carbonyl in hydantoin ring show at 1769 and 1706 cm^{-1}, pointing to the existence of ADMH. Bands at 1024, 1095 cm^{-1} are due to O–H bending. More importantly, characteristic carboxylic acid O–H bending at 1262 cm^{-1}, benzene C=C stretching at 1559 cm^{-1} and para-substituted benzene C–H bending at 803 cm^{-1} support the assignment of the ions series *m*/*z* 319, 487, 655. Since pure terephthalic acid has been separated into the "TPA Portion" and cannot go into the "Soluble Portion" if not linked with water soluble monomer ADMH. The analysis of the "TPA Portion" showed no evidence of grafting products.

3.4. Influence of reaction temperature and time on ADMH grafting polymerization

Since decomposition of initiator is solely determined by reaction duration and temperature, their impact on grafting polymerization was explored. PET fabric 10 g were soaked in 120 mL methanol containing 2.09 g BPO (8.65 mmol) and 2.91 g ADMH (17.3 mmol) for 24 h. Following such a long duration of soaking, the solution was dried on the surface of PET sample. Then, the samples with approximately 40% dry add-on were cured at 100 °C, 120 °C and 140 °C, respectively. Within the studied temperature and time range, the grafting yields are all below 1% (Fig. 6). Under both 100 °C and 120 °C, the grafting yield increases with time. However, for 140 °C series, the grafting yield levels off at 20 min and is even less than that of 100 °C and 120 °C.



Scheme 2. Possible pathways of radical reactions.

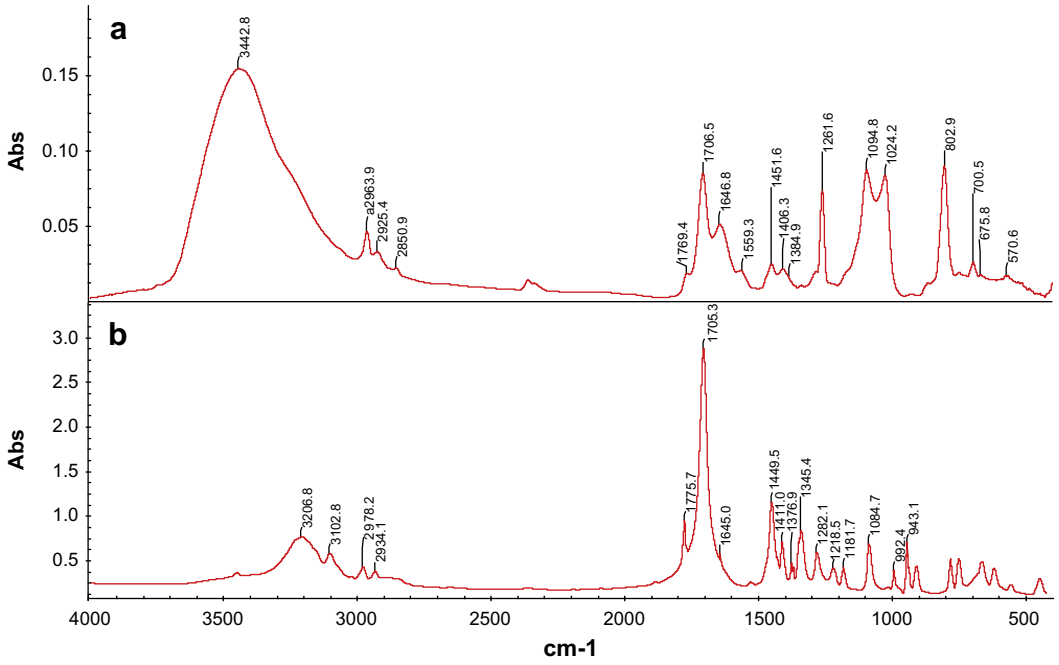


Fig. 5. IR spectra of (a) "Soluble Portion" (b) standard ADMH.

According to DSC study, ADMH itself does not decompose until reaching 160 °C. However, in a separate model study, decomposition of ADMH to 5,5-dimethylhydantoin was detected when ADMH was heated together with initiator at 140 °C. The decomposition of ADMH is a competing side reaction of grafting polymerization, and contributes to lower grafting yields at 140 °C for extended curing (20 min, 30 min).

3.5. Antibacterial test

The poly(ADMH) grafted PET fabric was converted to *N*-chloramide structure in a simple chlorination process – immersing the samples in a chlorine bleach solution (3000 ppm available chlorine) at room temperature for 30 min. The liquid to fabric (liquor) ratio was 50:1 (w/w). The fabrics were then rinsed in excess amounts of distilled water and air-dried. The chlorinated poly(ADMH)-*g*-PET sample was challenged with 10^5–10^6 CFU/mL *E. coli* (K 12). The results are listed in Table 1. Due to its hydrophobicity, the antibacterial performance of the chlorinated PADMH-*g*-PET fabric was not as good as the cotton counterpart [32]. With the extension of contact time, the reduction percentage of *E. coli* increased and a total kill of *E. coli* could be achieved at a contact time of 2 h.

Table 1
Antibacterial results of PADMH-*g*-PET fabrics.

	Active chlorine (ppm)	Percentage reduction of *E. coli* at different contact times (%)		
		30 min	60 min	120 min
Poly(ADMH)-*g*-PET	288	50%	96%	>99.999

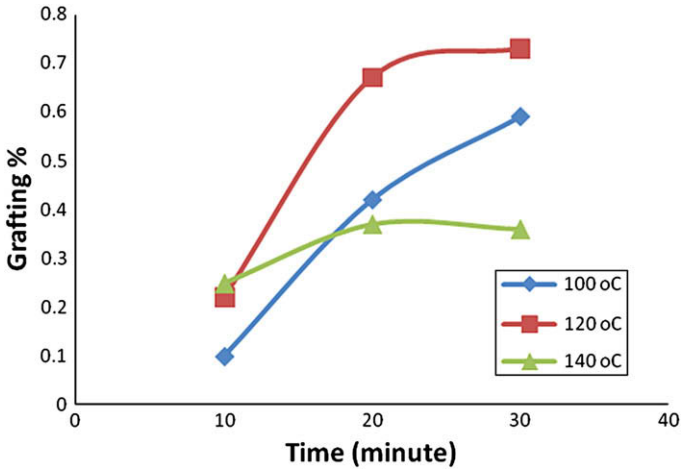


Fig. 6. Impact of reaction temperature and time on ADMH grafting.

4. Conclusions

Radical graft polymerization on polyester could be performed with benzoyl peroxide as an initiator. Benzoyl peroxide could generate macromolecular radicals on surfaces of polyester fibers. Methanol was used as a swelling agent to assist diffusion of the initiator and the monomer into polyester during the process. 3-Allyl-5,5-dimethylhydantoin (ADMH) was grafted onto PET fabrics and the reaction was proposed to be at the end of polyester chain and by a cleavage of the ester bond. After converted to *N*-chloramide structure, a poly(ADMH)-*g*-PET fabric can demonstrate total kill of 10^5–10^6 CFU/mL *E. coli* at the contact time of 2 h.

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