

Studies on Acrylic Acid–Grafted Polyester Fabrics by Electron Beam Preirradiation Method. I. Effects of Process Parameters on Graft Ratio and Characterization of Grafting Products

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ABSTRACT: Polyester fabrics were preirradiated by electron beam in air and then grafted by acrylic acid (AA) without excluding oxygen. Effects of preirradiation dose, monomer concentration, reaction temperature, storage time, sulfuric acid, and Mohr's salt were investigated in detail and are discussed. The results suggest that it is practicable and effective to graft AA onto polyester fabrics by means of the preirradiation method. FTIR and SEM were used to characterize AA-grafted polyester fabrics. A new band appearing at 1546 cm^{-1} in the FTIR spectrum implies that AA was

indeed introduced onto PET macromolecules. Changes of the diameter and the surface structure of fabric fibers presented in SEM micrographs make it clear that a layer of grafted poly(acrylic acid) was formed on the surface of these PET fibers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3931–3938, 2003

Key words: graft copolymerization; electron beam preirradiation; polyesters; acrylic acid; fibers

INTRODUCTION

In recent years, much interest has focused on the research of functional textiles, given that they are playing increasingly important roles in industry and people's daily lives. Modification of generally used fabrics and fibers is widely used to produce functional textiles for convenience and high efficiency. Modification can be carried out through different ways including, for example, dipping in chemical reagent,¹ surface treating with plasma,^{2–5} surface coating, and graft copolymerization.^{6–8}

One kind of polymer chain, which possesses or can produce a certain specific function, can be introduced to another kind of macromolecular backbone by chemical reaction, which is known as graft copolymerization. It is the linkage of covalent bond between the graft chains and the substrate macromolecules that guarantees the permanence of the modification. Graft copolymerization can be achieved by chemical initiators,^{9–14} ultraviolet light,^{15–17} or ionizing radiation.^{14,18–20}

Detailed studies in radiation grafting began in the 1950s.²¹ Radiation grafting is one of the most promising modification methods because of its unmatched advantages, for example, large penetration in polymer

substrate, rapid and uniform formation of active sites for initiating grafting throughout the substrate,¹⁸ and little pollution because it is environmentally benign, being free of chemical initiator and so forth. Both the direct method and the preirradiation method can be used in ionizing radiation grafting.

Because it is a relatively inert polymer, poly(ethylene terephthalate) (PET) is one of the most difficult to graft²²; it is not easy to obtain a high graft ratio by use of the usual methods. Ionizing radiation can activate PET macromolecular chains effectively and allow graft copolymerization to occur rather easily. A variety of reactive monomers have been tried to graft onto polyester material.¹⁹

In this study, acrylic acid (AA) was grafted onto polyester fabrics by the electron beam (EB) preirradiation method. The AA-grafted polyester fabrics were found to have good water vapor permeability and excellent water-impermeable ability, as will be reported in a companion study. Here, factors that affect graft ratio, such as preirradiation dose, monomer concentration, reaction temperature, storage time, sulfuric acid, and Mohr's salt are discussed in detail. In addition, FTIR and SEM were used to characterize the grafted fabrics.

EXPERIMENTAL

Materials

We used two types of polyester fabrics: (1) abbreviated as "D", T21s/2 × T21s/2 × 69 × 44.5 × 48"

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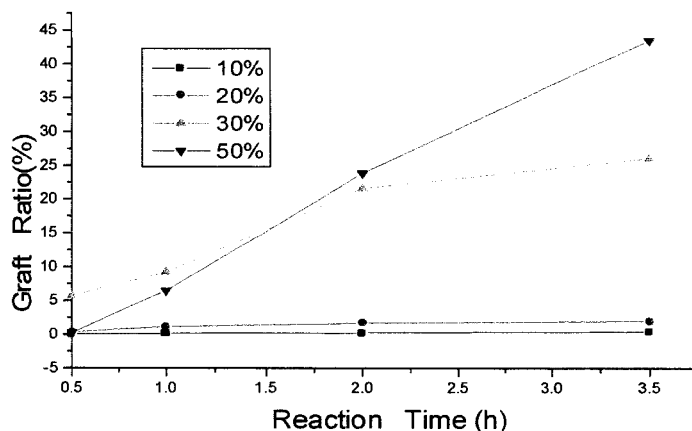


Figure 1 Effect of monomer concentration on graft ratio. Conditions: fabric, "D"; grafting temperature, 77°C.

(provided by Tianyi Textiles Group Co., Tianjin City, China); (2) abbreviated as "T", 75D/272F \times 150D/272F (provided by Cloth Plant of Yangzhou, China). AA was of analytical reagent grade (provided by Tianjin Institute of Chemical Reagents, China), containing 0.01–0.1% inhibitor, and was used without further purification. Mohr's salt and sulfuric acid were both analytical reagents.

Preirradiation

Polyester fabrics, which had been desized and boiled-out, were cut into round samples (diameter 90 mm). Each piece was then sealed in a polyethylene bag to be protected from contamination. The sample bags were set on a roller (diameter 1.1 m) that was rotating just under the EB window. The EB provider was a high-frequency and high-voltage Great Power Electron Accelerator (GJ-1.5 type; Accelerator Institute, Xianfeng Electrical Machinery Plant, Shanghai, China). General operation parameters were as follows: vacuum, 9.6×10^4 Pa; average beam current, 5 mA; approximate dose rate, 2.2×10^4 rad/s.

Grafting procedure

A definite amount of AA aqueous solution was introduced into a 100-mL stoppered conical flask in a temperature-controlled water bath. Some other kinds of reagent were also added, if needed, at the same time. The flask was immediately stoppered after the irradiated sample was introduced and the graft copolymer-

ization began. The reaction system was refluxed during the reaction.

When the desired reaction period was reached, the sample was taken out from the flask and rinsed repeatedly with water to remove homopolymer adhering to the sample, followed by extracting with boiled distilled water three times, and then dried to a constant weight in a vacuum oven.

Graft ratio

The graft ratio (G) was calculated using the following equation:

$$G = \frac{w_1 - w_0}{w_0} \times 100\%$$

where w_0 and w_1 are the weight of the original and the grafted polyester fabric sample, respectively.

Characterization

FTIR and SEM techniques were used to characterize the grafted products. Infrared spectra were obtained from a Nicolet 560 E.S.P. (Nicolet Analytical Instruments, Madison, WI) using the KBr pellet technique. Images of the fabric surface were taken using an XL30 environmental scanning electron microscope (ESEM; Philips, The Netherlands). A thin layer of gold was sprayed onto the sample surface before it was observed with SEM.

TABLE I
Effect of Reaction Temperature on Graft Ratio (I)^a

Monomer concentration (wt %)	10	20	30
Graft ratio (61°C) (%)	0.21	1.17	1.24
Graft ratio (70°C) (%)	0.09	1.60	9.19

^a The fabric was "T" and the reaction time was 1 h.

TABLE II
Effect of Reaction Temperature on Graft Ratio (II)^a

Reaction temperature (°C)	40	55	64	76
Graft ratio (%)	0	0	17.8	25.6

^a The fabric was "T" stored at -18°C for 252 h before graft; monomer concentration was 30 wt %; and reaction time was 7 h.

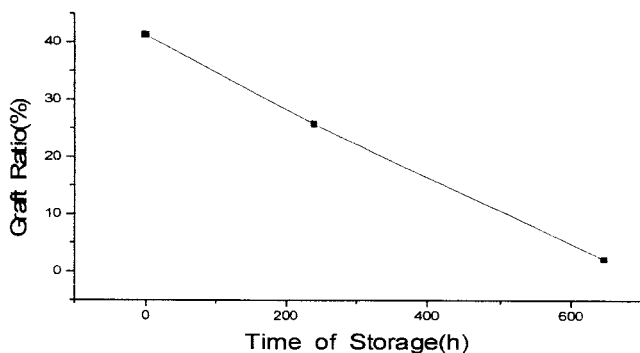


Figure 2 Effect of storage time on graft ratio. Conditions: fabric, "D"; storage temperature, -18°C ; reaction temperature, 75°C ; monomer concentration, 30 wt %; reaction time, 9 h.

RESULTS AND DISCUSSION

Effects of process parameters on graft ratio

Preirradiation dose

Of those factors that should be taken into consideration in graft copolymerization using the preirradiation method, the preirradiation dose is of primary importance because it plays an important role in both inducing grafting and destroying the polymer substrate. An adequate dose can efficiently activate the "dead" macromolecules of substrates and produce enough active sites on which graft copolymerization occurs; however, an excessive dose may cause polymer degradation (especially when the irradiation is carried out in air atmosphere) and deteriorate the appearance, mechanical strength, and other properties of the products. Actually, many researchers have discovered that the graft ratio increases with increasing dose within a certain range, and then decreases.¹⁹ We

found that the dose of 25 Mrad was suitable for our investigation after repeated attempts; thus, all irradiations in this work were carried out at this dose.

Monomer concentration

Results of many investigators^{18,23} indicated that the monomer concentration has a primary effect on the graft ratio. Figure 1 shows the effect of monomer concentration on graft ratio. The fabrics were introduced into the flask immediately after preirradiation (the procedure is the same for other figures unless otherwise indicated). From the curves, one may observe that the graft ratio rapidly reaches a constant value when the monomer concentration is low (≤ 20 wt %), whereas it increases gradually with time at higher monomer concentrations. The curves show a general trend: the higher the monomer concentration, the higher the graft ratio after the same reaction time. In other words, the grafting rate increases with increasing monomer concentration.

The grafting rate is controlled primarily by the diffusion of monomers. During nonhomogeneous graft copolymerization taking place between the liquid phase of the monomer and the solid phase of the polymer substrate, the diffusion of monomer involves two parts. One is the diffusion of the monomer within the reaction solution. The monomer concentration around the substrate decreases gradually as a result of the consumption of monomer as grafting copolymerization proceeds; thus, the monomer nearby has to diffuse here from areas of higher concentration. The other is the diffusion of monomer toward the substrate interior. At the early stage of grafting, the monomer reacts with the active sites on the substrate and the substrate surface is gradually covered with the

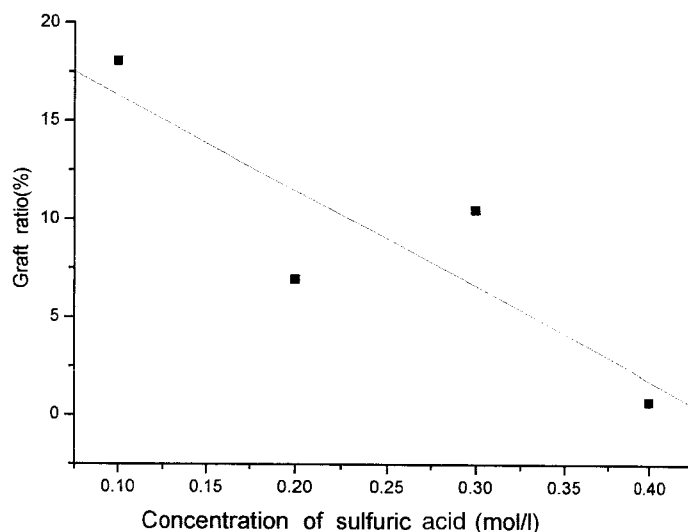


Figure 3 Effect of sulfuric acid on graft ratio. Conditions: fabric, "T"; reaction temperature, 75°C ; monomer concentration, 30 wt %; reaction time, 9 h.

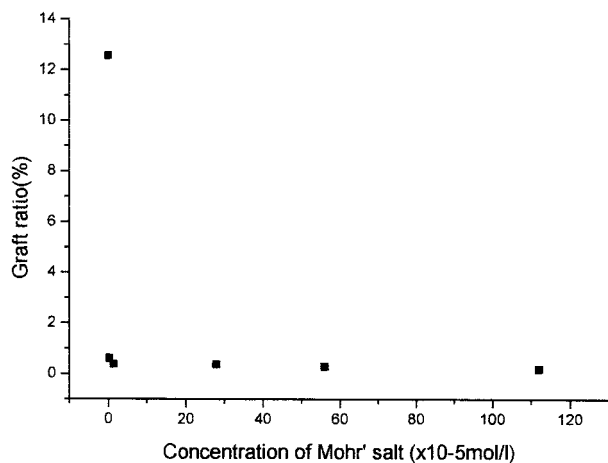


Figure 4 Effect of Mohr's salt concentration on graft ratio (I). Conditions: fabric, "T"; reaction temperature, 75°C; monomer concentration, 30 wt %; reaction time, 7.3 h.

graft chains. The monomer then has to diffuse into the interior of the substrate to react with free radicals in the sublayer and the short propagating chains sheltered by other grafting chains formed earlier. It is obvious that both rates of the two parts of the diffusion increase with increasing monomer concentration, which result in the increase of the grafting rates. It must be realized that the increase of the monomer concentration does not always benefit the enhancement of grafting rate and graft ratio because of the simultaneous increase of the viscosity of the reaction system resulting from the formation of the poly-(acrylic acid) (PAA) homopolymer, which will dramatically slow down the diffusion of the monomer.

Grafting temperature

Table I and Table II show the effects of reaction temperature on graft ratio. In the reaction system of preir-

radiation initiation grafting, the effects of temperature are complicated. It is well known that the initiating centers are mainly peroxide and hydroperoxide groups when polymer substrates are preirradiated in air. Temperature is the primary dynamic parameter of the decomposition of peroxide and hydroperoxide groups into free radicals. Higher temperatures can accelerate the formation of free radicals through the decomposition of these groups, which will increase the grafting rate and the graft ratio. In addition, temperature is the essential dynamic parameter of the grafting copolymerization: higher temperature benefits copolymerization. Moreover, temperature helps homopolymerization, which is a competitive reaction to graft copolymerization. Thus, the effects of temperature should be considered broadly. In this study, grafting did not take place below 55°C, and the graft ratio increased with temperature in general.

Storage time

Active centers produced by preirradiation can remain active for a certain time in an appropriate environment, although they will vanish gradually as storage time lengthens. According to Li et al.,²⁴ peroxide of silicon rubber decomposes gradually when exposed to air, and the rate of decomposition is essentially influenced by temperature. In this study, the effect of storage time on graft ratio is shown in Figure 2. From the figure we can see that the graft ratio decreases linearly with storage time, which was unlike results in the work of other researchers.²⁵ This inconsistency may be a result of the difference of polymer substrates used.

Sulfuric acid

Inorganic acid is often used as an additive in grafting reaction systems.²¹ It is considered that the acid

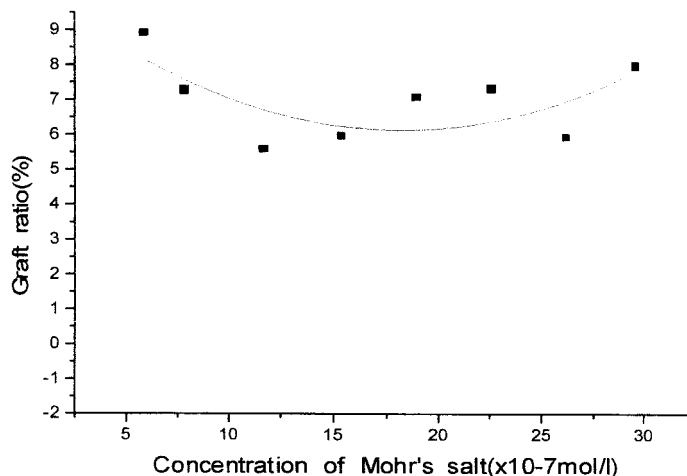
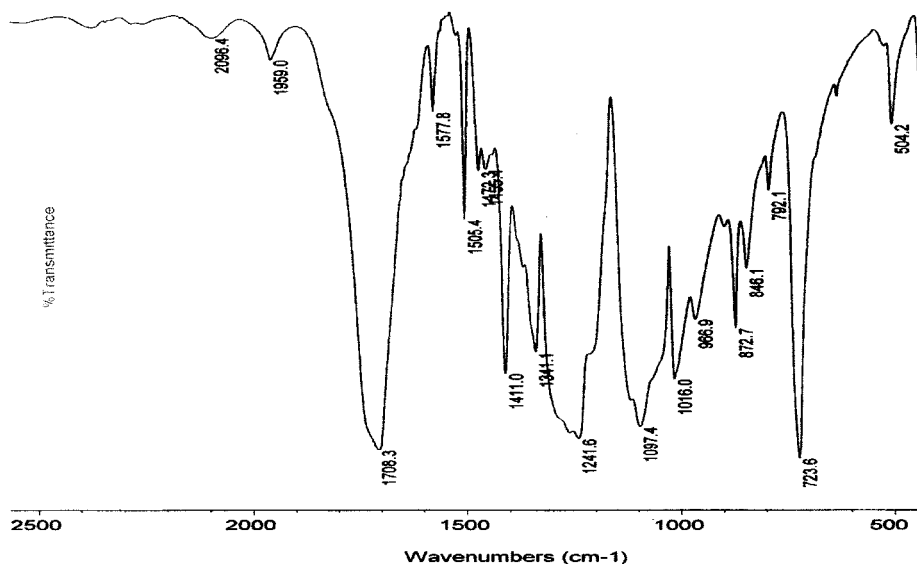
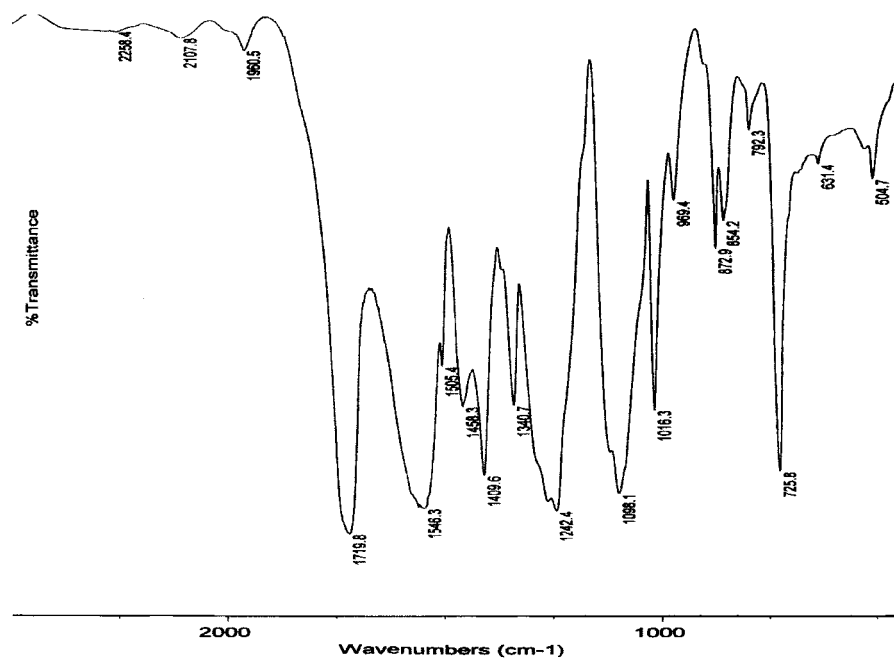


Figure 5 Effect of Mohr's salt concentration on graft ratio (II). Conditions: fabric, "D"; reaction temperature, 77°C; monomer concentration, 30 wt %; reaction time, 9 h.



(a)



(b)

Figure 6 FTIR spectra of polyester fabrics before and after grafting by AA: (a) EB preirradiated fabric; (b) AA-grafted fabric.

affects the grafting reaction process by influencing the free-radical mechanism. Figure 3 shows the effect of the sulfuric acid concentration on the graft ratio. The addition of sulfuric acid dramatically decreased the graft ratio, and the higher the sulfuric

acid concentration, the greater the decrease in the graft ratio. The observation of the reaction process showed that sulfuric acid strongly promoted homopolymerization, which resulted in increasing viscosity of the reaction system, thus greatly depress-

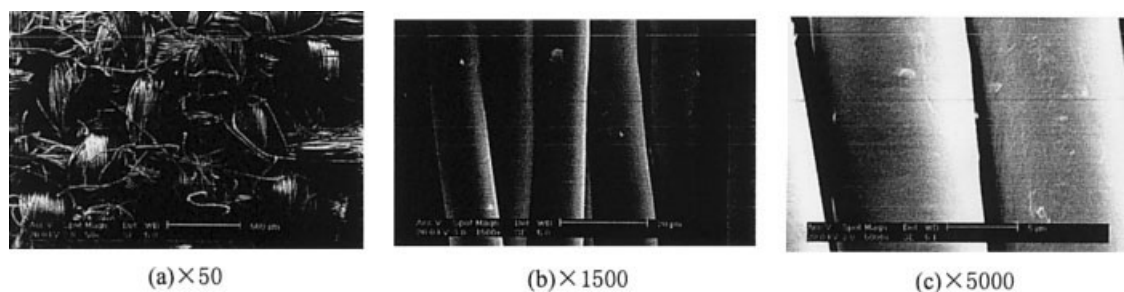


Figure 7 SEM micrographs (a)–(c) of original polyester fabrics.

ing the diffusion of the monomer toward grafting sites.

Mohr's salt

Mohr's salt^{24–26} or other kind of reducible inorganic salt such as CuSO_4 ²⁷ or CuCl_2 ²⁸ have been employed in many grafting reaction systems. Reducible inorganic salt is one of the most important and complicated factors in preirradiation grafting systems. The role of Mohr's salt in graft copolymerization is discussed in detail.

First, it can make the grafting reaction occur at a lower temperature. It was stated above that, in preirradiation grafting systems, free radicals are generated from the decomposition of peroxide and hydroperoxide groups, which are significantly affected by reaction temperature. Therefore, the temperature often needs to be increased to enhance the grafting rate. However, increasing temperature will inevitably accelerate homopolymerization. With the help of Mohr's salt, the thermal decomposition reaction from which free radicals are produced can be displaced by the following redox reaction²⁵:

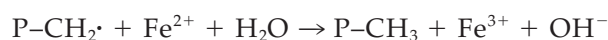
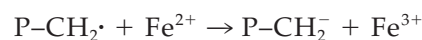


This will enable grafting at a relatively low temperature.

Second, it can act as an inhibitor of homopolymerization. The thermal decomposition of hydroperoxide is



$\text{OH}\cdot$ can then initiate the homopolymerization of the monomer. No $\text{OH}\cdot$ is produced in the redox reaction involving Fe^{2+} ; thus homopolymerization could be effectively restrained. Moreover, the monomer free radicals and the active homopolymer propagating chain free radicals can also be partly inhibited or even deactivated.^{26,29}



Thus homopolymerization is inhibited to some extent.

Third, it can serve as an inhibitor of the chain propagation reaction of graft copolymerization. Because free radicals of homopolymer-propagating chains can be deactivated by Fe^{2+} , it also has the same inhibition influence on grafting chain free radicals simultaneously. However, because of the heterogeneous reaction for grafting on a solid polymer substrate in a liquid monomer, the concentration of Mohr's salt in the solid substrate is much lower than that in the monomer solution. Thus inhibition of grafting should be much weaker than that of homopolymerization.

The effect of Mohr's salt is given in Figure 4. The sharp transition at 2.8×10^{-6} mol/L and the consequent leveling off of the curve indicate that the Mohr's salt concentration of 2.8×10^{-6} mol/L is enough to restrain both homopolymerization and grafting dramatically. Continuous experiments in the concentration range of 5.91×10^{-7} to 2.96×10^{-6} mol/L were carried out and the results are given in Figure 5. It may be seen that the concentration in this range has a similar effect on the graft ratio. The higher the concentration of Mohr's salt, the more effectively it restrains homopolymerization, but at the same time it exerts a significant influence on graft copolymerization and decreases the graft ratio. It is necessary to use Mohr's salt in the grafting reaction system from the consideration of saving monomer. It is also possible and feasible to achieve a desired graft ratio by the careful selection of Mohr's salt concentration and other reaction parameters.

Characterization of grafting products

FTIR characterization

Infrared spectra of the preirradiated and grafted fabrics are presented in Figure 6. The appearance of a new band at 1546 cm^{-1} , which is assigned to the vibration of COO^- , suggested that the AA uniting

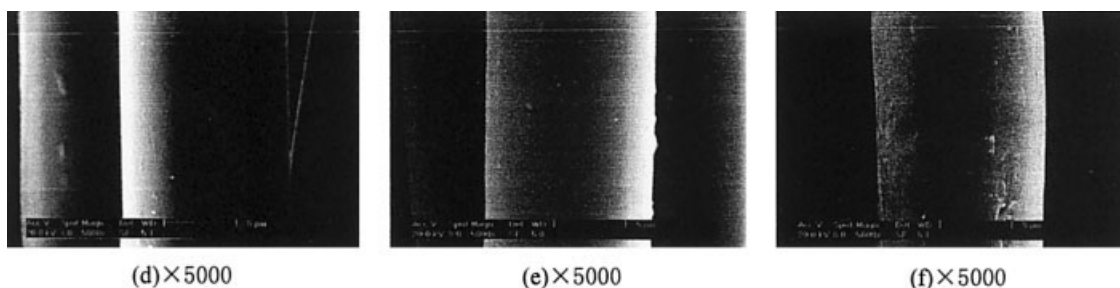


Figure 8 SEM micrographs of preirradiated polyester fabrics. Preirradiation dose: (d) 25 Mrad; (e) 50 Mrad; (f) 75 Mrad.

with the $-\text{COOH}$ group was indeed introduced onto the PET macromolecular backbone.

SEM characterization

SEM micrographs of the original and preirradiated fabrics are presented in Figure 7 and Figure 8, respectively, from which one may observe that the fibers of fabrics appear in the form of a regular columnlike shape and their surfaces are neat and smooth. It can be concluded that the shape and surface of the fibers did not undergo any evident changes after preirradiation.

Figure 9 shows SEM micrographs of AA-grafted fabric (graft ratio was 22.3%) that are remarkably different from those of the original and preirradiated fabrics. The fibers no longer present a regular columnlike shape and their surfaces are covered with a layer of PAA that is grafted with PET macromolecules. Furthermore, there are many protrusions scattered on the grafted layer, which make the surfaces rough and coarse rather than neat and smooth. It also can be seen that the diameter of fibers increases by about 30–50% because of the grafted layer.

Figure 10 shows SEM micrographs of the residue of *m*-cresol-treated AA-grafted fabric. We can see from (j) that the residue retains the original sheaflike structure of yarns from which the fabric is made. Micrographs (k), (l), and (m) are of fibers from (j) at higher magnifications, although these strips are shriveled and flat instead of plump and smooth. Apparently, the interior of fibers has been dissolved away and only the exterior shell remains to keep a fibrous shape.

With regard to solubility, a graft copolymer could not usually dissolve either in a good solvent of the main-chain polymer or in that for homopolymer of the graft monomer. *m*-Cresol is a good solvent for polyester. The change from “plump columns” to “shriveled strips” indicates that the PET composition inside the grafted fibers was dissolved away by *m*-cresol, whereas the grafting layer outside the fibers is left and basically keeps a fibrous shape, given that the graft reaction occurs only on the surface. These micrographs dramatically illustrate that a grafting layer of PAA has been formed on the surface of PET fibers.

In addition, this method—a combination of solvent treating and SEM observations (it could be named the “dissolution-SEM” method)—is feasible and effective to study and characterize grafted fibrous materials.

CONCLUSIONS

The effects of reaction conditions on graft ratio based on “AA-preirradiated polyester fabrics” reaction systems were investigated in detail. It was found that a longer reaction time, higher reaction temperature, and a greater monomer concentration can bring about higher graft ratios, whereas the effects of storage time and sulfuric acid on the graft ratio are the opposite. Mohr’s salt can enable grafting at a lower temperature, and at appropriate concentrations it can effectively inhibit homopolymerization.

FTIR and SEM were employed to characterize polyester fabrics grafted by AA. In the IR spectra of grafting products, a new band at 1546 cm^{-1} , which is assigned to

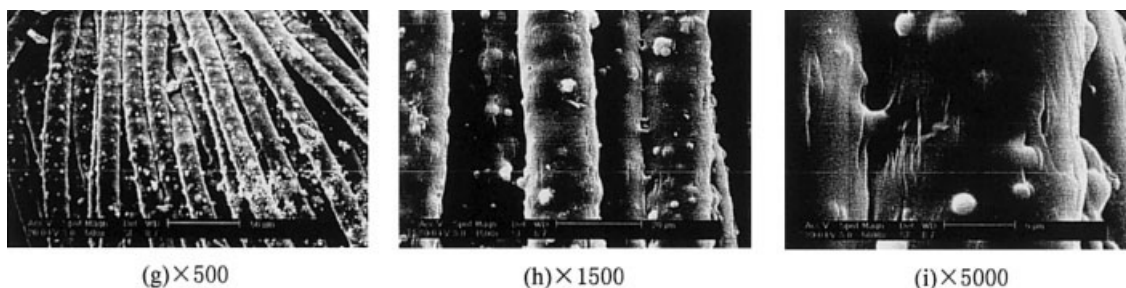


Figure 9 SEM micrographs (g)–(i) of AA-grafted fabrics (graft ratio is 22.3%).

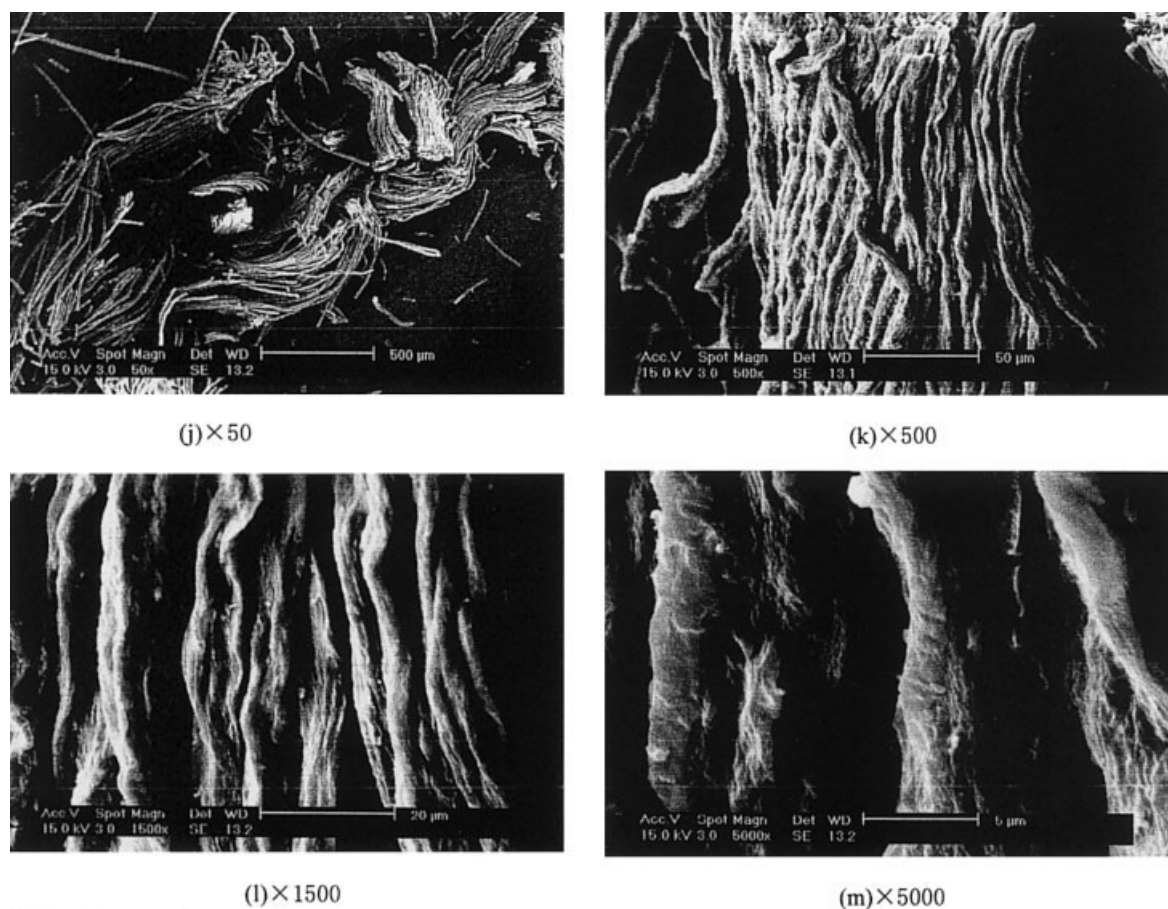


Figure 10 SEM micrographs (j)–(m) of the residue of *m*-cresol-treated AA-grafted fabric.

the COO^- group, indicates that AA monomer units were indeed introduced onto the PET macromolecule backbone. SEM micrographs show direct and vivid differences between the original and the grafted fabrics, which reveal that a layer of grafted PAA coating was formed on the surface of the fibers of the fabrics. Moreover, the “dissolution-SEM” method is a promising way to characterize grafted fibrous materials.

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