Thermal and Flame-Retardant Properties of Polyester Fabric Grafted with Polyanilines

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ABSTRACT: The chemical grafting of polyaniline, poly(*o*-anisidine), and poly(*o*-toluidine) on polyester fabric was carried out with ammonium peroxodisulfate in an acidic medium. The formation of the grafted fabric substrate was confirmed with reflectance spectroscopy, Fourier transform infrared spectroscopy, weight-loss studies, and conductivity measurements. The grafting percentage and efficiency percentage were determined for the different grafted substrates. The thermal and flame-retardant properties of these grafted substrates were elucidated. Thermogravimetric analysis thermograms and derivative thermogravimetry curves showed that the grafted substrates had a higher thermal stability and char-residue percentage at 700°C. The grafted substrates showed a higher activation energy of thermal decomposition than the nongrafted substrates. The grafted substrates showed good flame retardancy, which was evident from the increase in the limited oxygen index in comparison with that of the nongrafted substrate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1981–1988, 2004

Key words: conducting polymers; degradation; flame retardance

INTRODUCTION

Textile fibers are modified via graft polymerization techniques for certain end-use applications. Recently, Kawahara et al.[1] grafted methyl acrylamide onto silk fibers and studied the structure and mechanical properties of the grafted fibers. Sacak and coworkers[2,3] modified the mechanical and thermal properties of poly(ethylene terephthalate) (PET) fibers through the graft copolymerization of various vinyl polymers onto PET fibers. Gopalan et al.[4] grafted polyacrylonitrile onto PET and nylon-6 fibers initiated by a redox system.

Since the discovery of the metallic properties of molecularly doped polyacetylene, there has been rapid growth in the field of electronically conducting polymers. Among the known electronically conducting polymers, polyaniline (PANI) and its derivatives have emerged as the most important class of compounds. PANI and its derivatives are interesting because of the presence of chemically flexible —NH— groups in the polymer backbone, which not only take part in the protonation–deprotonation process but also contribute to the π-band formation, ensuring greater environmental stability.[5]

PANI and its derivatives can be obtained by chemical or electrochemical methods.[6] Although they are easily synthesized in the bulk, their use is restricted because of their nonprocessability by normal melt or solution techniques. Applications such as the control of electromagnetic interference (EMI)[7] and the dissipation of electrostatic charge (ESD)[8] require a thin conducting film or coating on a flexible surface or substrate.

With this objective, we decided to prepare thin films or coatings of PANI and its derivatives on flexible substrates such as fabrics. There are earlier reports of the graft copolymerization of conducting polymers onto various surfaces. The grafting of PANI onto a poly(amino styrene) backbone was reported by Li et al.[9] The graft copolymerization of polythiophene onto poly(methyl methacrylate) was reported by Sunke et al.[10] Anbarasan et al.[11] reported the graft copolymerization of PANI onto PET fibers.

We report here the synthesis, characterization, thermal, and flame-retardant properties of polyester fabrics grafted with PANI, poly(*o*-anisidine) (POAN), and poly(*o*-toluidine) (POT), which can be exploited for the aforementioned applications.

EXPERIMENTAL

Materials

All the chemicals were analytical-reagent-grade. Aniline, *o*-anisidine, and *o*-toluidine were distilled twice *in vacuo* before use. All the other chemicals were used

TABLE I
Graft Parameters, Direct-Current conductivity, and Thermal Decomposition Kinetic Data of the Grafted and Parent Nongrafted Substrates

Substrate	Grafting (%)[a]	Efficiency (%)[a]	Conductivity (S cm^{-1})[b]	For the first major weight-loss step (300–500°C)			For the second major weight-loss step (500–600°C)		
				E (kJ/mol^{-1})[c]	n[d]	R[e]	E (kJ/mol^{-1})[c]	n[d]	R[e]
PET	—	—	$<10^{-10}$	117.70	1.75	0.9985	240.62	0.88	0.9998
PANI-g-PET	11.41	5.59	5.00×10^{-3}	227.76	2.33	0.9992	1280.69	3.06	0.9639
POT-g-PET	8.62	3.81	2.94×10^{-3}	158.42	2.17	0.9986	515.68	2.30	0.9994
POAN-g-PET	3.84	1.30	0.44×10^{-3}	147.25	2.00	0.9966	387.89	1.55	0.9998

[a] [Monomer] = 0.3M; [oxidant] = 0.33M; [HCl] = 0.25M.
[b] S = Siemens (1 S = 1 Ω^{-1}).
[c] Calculated by the Friedman technique with a plot of -ln($d\alpha/dt$) versus $1/T$.
[d] Calculated by the Kissinger technique.
[e] Linear correlation coefficient.

as supplied. The polyester (PET) fabric was a gift from the Textile Department of the Institute of Chemical Technology (Mumbai, India). The fabric was Soxhlet-extracted with acetone for 24 h and was used after it was dried at room temperature.

Instruments

The reflectance spectra of the grafted substrates were obtained on a Data Color International reflectance spectrophotometer. The samples were scanned at wavelengths of 400–700 nm. The reflectance spectra were obtained for both the PET substrates grafted with HCl-doped PANIs and the PET substrates grafted with dedoped PANIs. The PET substrates grafted with HCl-doped PANIs, which were green, were treated with a 0.1N NH$_3$ solution for 24 h; this yielded grafted PET substrates dedoped with NH$_3$ (which were blue).

The Fourier transform infrared (FTIR) transmission spectra of the grafted and parent nongrafted polyester fabrics were recorded on a Nicolet FTIR Magna 550 spectrometer at a 2-cm^{-1} resolution. For comparison, the FTIR spectra of authentic HCl-doped PANI, POAN, and POT were also recorded.

The flame retardancy of the grafted and parent nongrafted substrates was measured in terms of the limited oxygen index (LOI) according to ASTM D 2863-77.

The thermogravimetric analysis (TGA) thermograms and derivative thermogravimetry (DTG) and second-derivative thermogravimetry (2DTG) curves of the substrates were obtained on Mettler TA 4000 system thermogravimetric instrument at a heating rate of 10°C/min under a nitrogen atmosphere and over a temperature range of 40–700°C.

The direct-current conductivity of the substrates was measured by the conventional two-probe technique according to the method used by Anbarasan et

al.[12] A 1-cm length of a fiber was taken out from the grafted fabric substrate and attached between the two probes of the instrument before the current was passed.

Grafting procedure

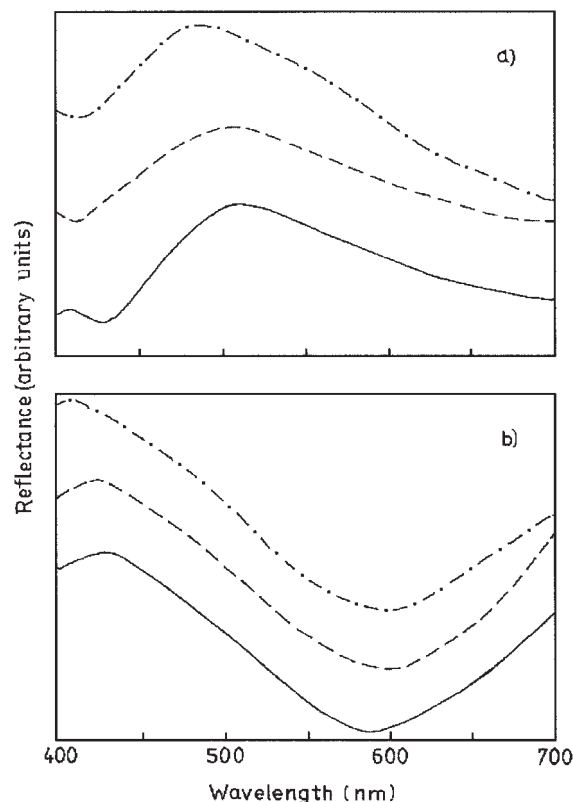Polyester fabric (PET) was thoroughly cleaned and dried before being subjected to the grafting process.

Figure 1 Reflectance spectra of (a) PET substrates grafted with HCl-doped PANIs and (b) PET substrates grafted with dedoped PANIs: (-●-) PANI-g-PET, (—) POT-g-PET, and (- - -) POAN-g-PET.
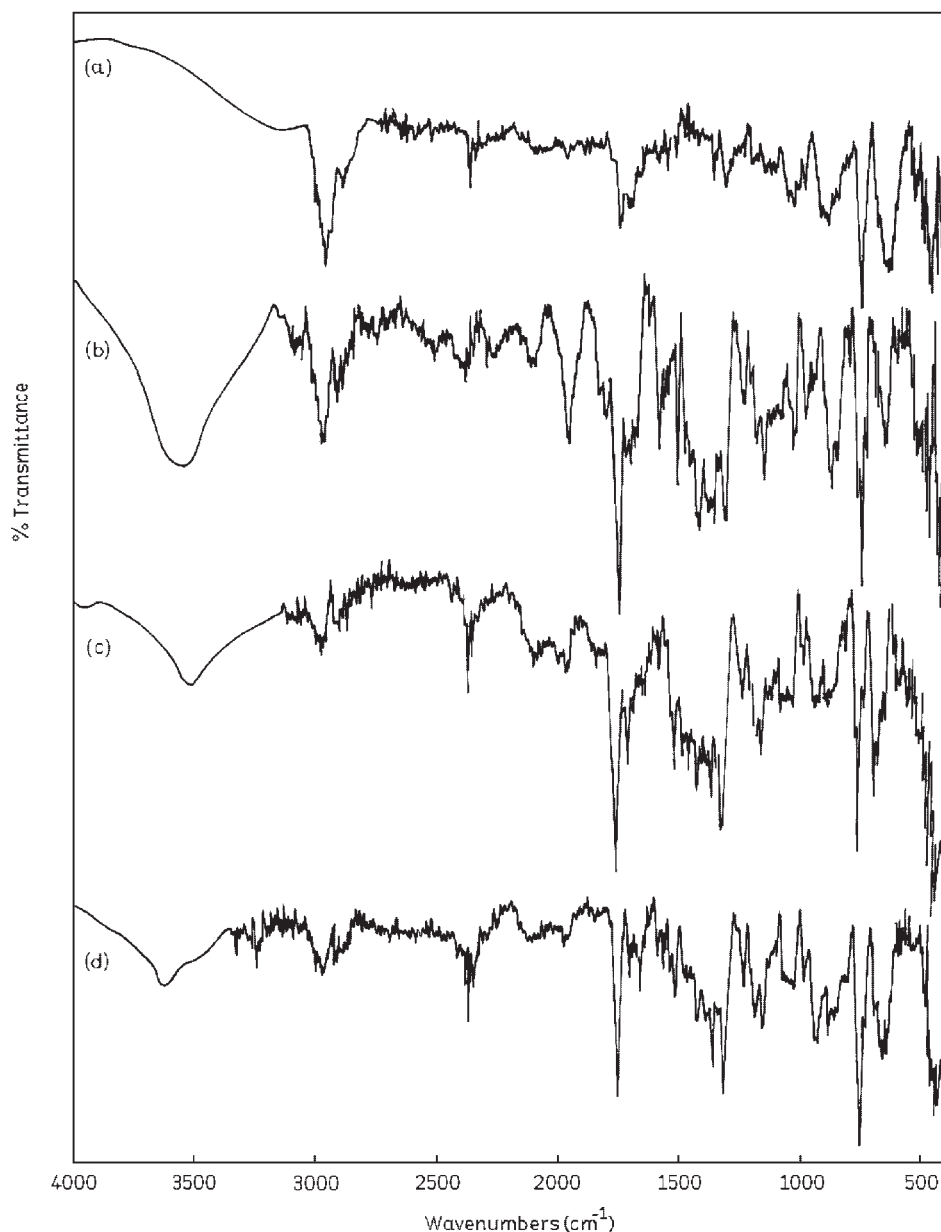
Figure 2 FTIR spectra of (a) PET, (b) PANI-*g*-PET, (c) POAN-*g*-PET, and (d) POT-*g*-PET.

The grafting of conducting PANI, POAN, and POT was carried out through the immersion of a PET substrate (15 cm × 15 cm) with an initial weight of W_1 (g) in solutions of 0.3M aniline, *o*-anisidine, and *o*-toluidine, respectively, in 0.25M HCl. The contents were then cooled to 0–5°C with an ice bath. After cooling, a stoichiometric amount of a chilled 0.33M solution of ammonium peroxodisulfate [$(NH_4)_2S_2O_8$] in 0.25M HCl was added to the reaction vessel. Because of the exothermicity of the reaction, the rate of addition of the oxidant solution was maintained in such a way that the temperature of the reaction mixture was always below 5°C. During the addition of the oxidant, the PET substrate was kept under constant stirring to ensure the uniformity of the reaction at the solid–solution interface. The reaction was continued for a total of 3 h. Upon the completion of the reaction, the grafted substrate was removed and thoroughly rinsed with distilled water. The grafted substrate was then treated with *N*-methyl-2-pyrrolidone (NMP) to remove any nongrafted polymer still adhering to the substrate. The grafted substrate was then thoroughly rinsed with distilled water. The final washing of the grafted PET substrate was performed through its immersion in a 0.25M HCl solution for 30 min. The substrate was then removed and dried at 50°C to a constant weight. The final weight of the dry grafted substrate was denoted W_2 (g). Each grafted substrate

TABLE II
IR Absorption Bands for the Grafted and Nongrafted Fabric Substrates

PET (cm^{-1})	PANI-*g*-PET (cm^{-1})	POAN-*g*-PET (cm^{-1})	POT-*g*-PET (cm^{-1})	Assignment
743	746	745	746	Out-of-plane C—H bending
—	830	824	827	Out-of-plane C—H bending of the *p*-disubstituted benzene ring
—	1153	1153	1153	Likely vibration of the charge defect (of the dopant Cl^- anion)
1301	1306	1316	1316	C—O stretching mode of the ester group
—	1500	1510	1510	Ring-mode vibration of the benzenoid structure
—	1601	1610	1612	Ring-mode vibration of the quinonoid structure
1744	1744	1744	1749	C=O stretching vibration of the ester group
2965	2971	2966	2981	C—H stretching vibration
—	3500	3500	3530	N—H stretching vibration band

was named according to the monomer taken for the graft polymerization: PANI-grafted polyester fabric (PANI-*g*-PET), POAN-grafted polyester fabric (POAN-*g*-PET), and POT-grafted polyester fabric (POT-*g*-PET).

For comparison, authentic samples of PANI, POAN, and POT were prepared according to the procedure given by Cao et al.[13] through the chemical oxidation of aniline in an aqueous HCl medium with ammonium peroxodisulfate as the oxidant (monomer/oxidant ratio = 1:1.1).

Rate measurements

The grafting percentage and efficiency percentage were calculated as follows:

$$\text{Grafting percentage} = (W_2 - W_1)/W_1 \times 100$$

$$\text{Efficiency percentage} = (W_2 - W_1)/W_m \times 100$$

where W_m is the weight of the monomer.

RESULTS AND DISCUSSION

Weight-loss study

The grafted PET substrate (X g) was soaked with $0.5N$ NH_3 for 12 h. This dedoped substrate was removed from the reaction mixture and dried at room temperature to a constant weight (Y g). The difference between X and Y was the change in the weight due to the dedoping of HCl from the grafted PET substrate. This dedoped substrate was again treated with NMP for 3 h, removed from the solution, dried *in vacuo*, and weighed. No weight loss was observed during the treatment with NMP. This indicated that any nongrafted PANIs still adhering to the substrate were completely removed from the PET substrate surface after the treatment with NMP during the grafting procedure, and the leftover weight apart from the

weight of the PET substrate was due to grafted side chains of the respective PANIs.

Mechanism of grafting

During the chemical oxidative polymerization of aniline, the polymer invariably films the walls of the reaction vessel. This behavior of conducting polymers was used here to graft the polymer onto an insulating
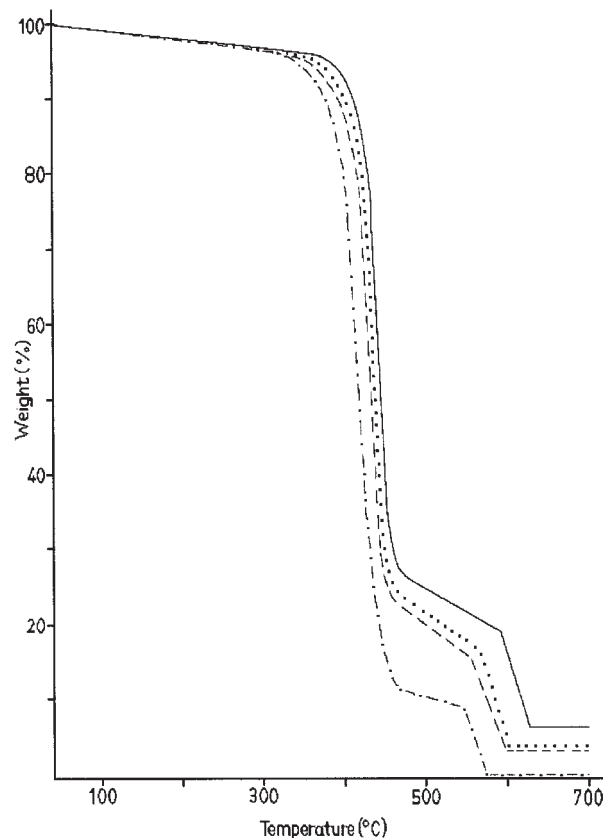

Figure 3 TGA thermograms of (---) PET, (—) PANI-*g*-PET, (···) POT-*g*-PET, and (– – –) POAN-*g*-PET.

TABLE III
Weight-Loss and Char-Residue Data for the Grafted and Nongrafted Substrates

Substrate	Step	Temperature range (°C)	Weight loss during the step (%)	Char residue at the end of the step (%)	Char residue at 700°C (%)
PET	I	90–300	2.50	97.00	
	II	300–490	85.75	11.25	0.4
	III	553–584	8.50	0.40	
PANI-*g*-PET	I	90–300	3.00	96.50	
	II	300–490	70.75	25.75	6.90
	III	577–625	13.10	6.90	
POAN-*g*-PET	I	90–300	3.25	95.75	
	II	300–490	75.00	20.75	3.75
	III	555–595	11.75	3.75	
POT-*g*-PET	I	90–300	3.60	95.40	
	II	300–490	73.40	22.0	4.50
	III	554–593	12.50	4.50	

substrate such as PET through the immersion of the substrate in the reaction mixture before the addition of the oxidant. It is proposed that during the reaction, cations of intermediate stability are adsorbed onto the surface and interstices of the fabric substrate and that these cations upon further radical coupling lead to stable, uniform, and adherent con-

ducting films. A probable mechanism for the peroxodisulfate-initiated graft copolymerization of aniline on wool fibers was proposed by Anbarasan et al.[14] and Bhadani et al.[15]

Grafting and efficiency percentage measurements

Both the grafting and efficiency values were greater for PANI-*g*-PET than for POAN-*g*-PET and POT-*g*-PET, as indicated in Table I.

Reflectance spectroscopy

The reflectance spectra of PET substrates grafted with HCl-doped PANIs and PET substrates grafted with dedoped PANIs are shown in Figure 1. The PET substrates grafted with HCl-doped PANIs show absorption bands at 415 nm for PANI-*g*-PET, at 411 nm for POAN-*g*-PET, and at 426 nm for POT-*g*-PET substrates. These bands around 420 nm (2.95 eV) are associated with radical cations indicating polarons as charge carriers and represent the conducting form of
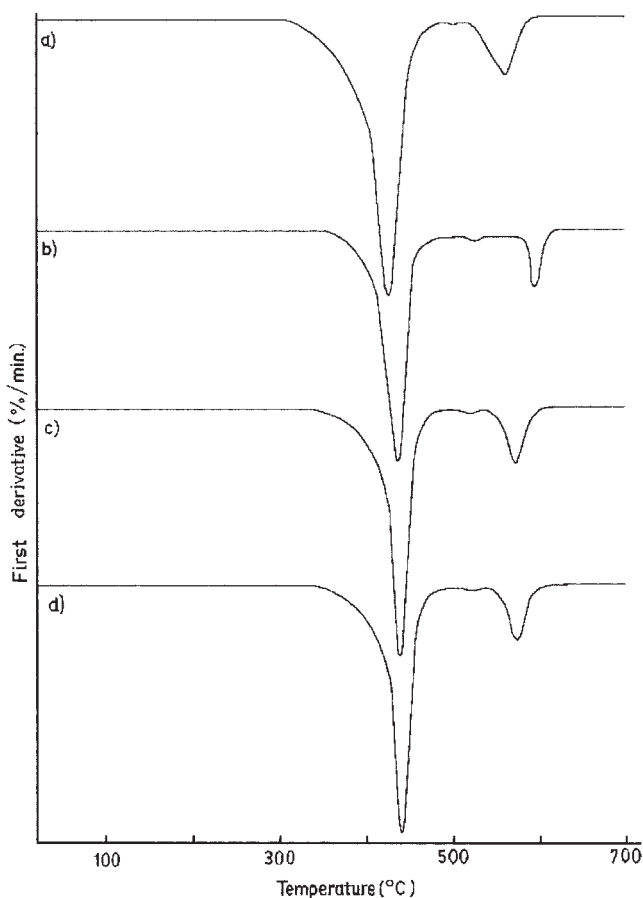
Figure 4 DTG thermogram curves of (a) PET, (b) PANI-*g*-PET, (c) POAN-*g*-PET, and (d) POT-*g*-PET.

TABLE IV
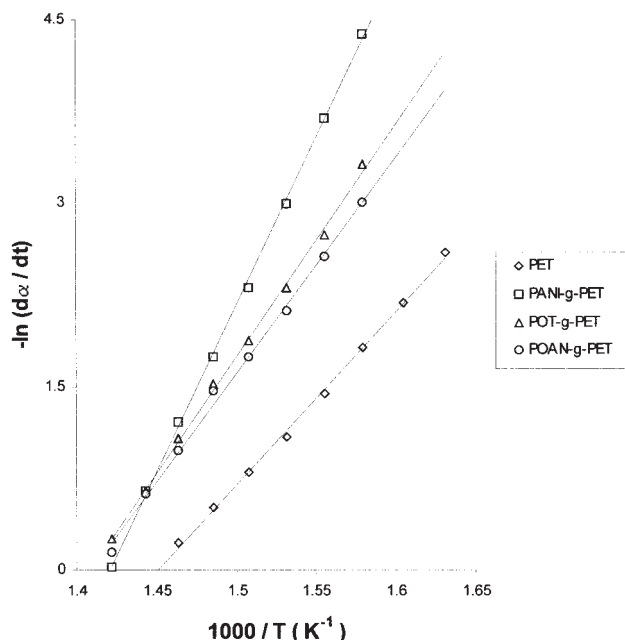**Decomposition Temperature Data for the Grafted and Nongrafted Substrates**

Substrate	Decomposition temperature (°C)		
	T_i	T_m	T_f
PET	300	430	489
	553	564	584
PANI-*g*-PET	310	438	494
	577	598	625
POAN-*g*-PET	303	436	501
	556	575	598
POT-*g*-PET	300	438	505
	554	574	593

T_i = temperature at the start of the weight-loss step; T_m = temperature at the maximum weight loss; T_f = temperature at the end of the weight-loss step.
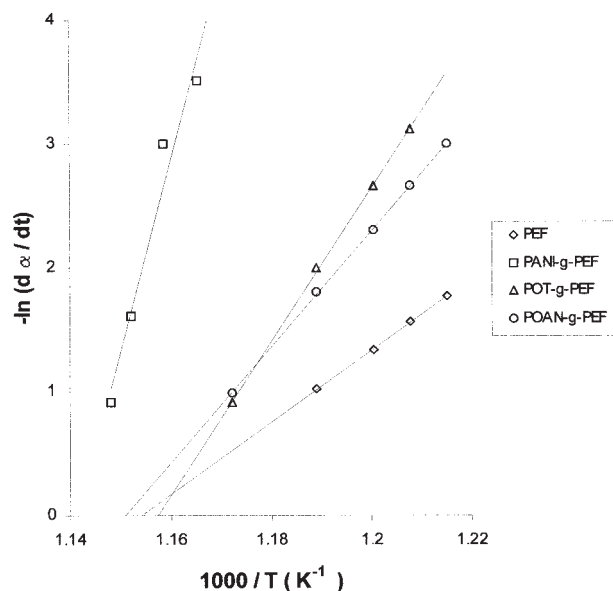
the grafted PANIs. The grafted substrates dedoped with NH_3 show the disappearance of the band around 420 nm and the appearance of a new absorption band at 602 nm for PANI-*g*-PET, at 590 nm for POAN-*g*-PET, and at 607 nm for POT-*g*-PET. The rise of this 600 nm (2.06 eV) band in the case of PET substrates grafted with dedoped PANIs correlates with the conversion of the conductive form of the respective PANIs to the oxidized, insulating form during the dedoping process.[16] These changes in the absorption bands of the grafted PET substrates due to the dedoping process confirm the grafting of respective PANIs onto the PET substrate.

FTIR spectroscopy

The FTIR spectra of the grafted and parent nongrafted polyester fabric substrates are shown in Figure 2. The grafted substrates PANI-*g*-PET, POAN-*g*-PET, and POT-*g*-PET show absorption bands similar to those observed for authentic HCl-doped PANI, POAN, and POT, respectively. The grafted PET substrates show vibrational bands around 825 cm^{-1} due to out-of-plane C—H bending of the p-disubstituted benzene ring, around 1150 cm^{-1} due to vibrations of the charge defect (of the dopant Cl^- anion), at 1500 cm^{-1} due to the ring-mode vibration of the benzenoid structure, at 1650 cm^{-1} due to the ring-mode vibration of the quinonoid structure, and around 3500 cm^{-1} due to N—H stretching vibrations. In addition, the spectra also

Figure 6 Friedman method $[-\ln(d\alpha/dt)$ vs $1/T]$ for the calculation of the activation energy of the thermal degradation of grafted and nongrafted substrates for the second major weight-loss step (550–600°C).

show some additional bands due to the polyester fabric backbone around 740 cm^{-1} due to out-of-plane C—H bending, around 1310 cm^{-1} due to C—O stretching, around 1745 cm^{-1} due to C=O stretching, and around 2971 cm^{-1} due to C—H stretching. This fact confirms the chemical grafting of polymer units onto the polyester backbone. The major absorption bands are listed in Table II.

Conductivity measurements

The conductivity values were determined for both grafted and nongrafted polyester fabrics (Table I). PANI-*g*-PET had higher conductivity than both POAN-*g*-PET and POT-*g*-PET. That the conductivity of all three grafted polyester substrates was higher than that of the parent nongrafted polyester substrates confirms the grafting process.

Thermal properties

TGA

Figure 3 shows the TGA thermograms of the grafted and parent nongrafted polyester substrates. All the substrates showed a small initial weight loss (ca. 2–4%) between 90 and 300°C, which may be explained by the evaporation of water molecules and the loss of the acid dopant (HCl) for grafted substrates bound to the polymer chain. The grafted and parent nongrafted substrates exhibited a two- or three-step weight loss. The first major weight loss (ca. 70–80%), between 300
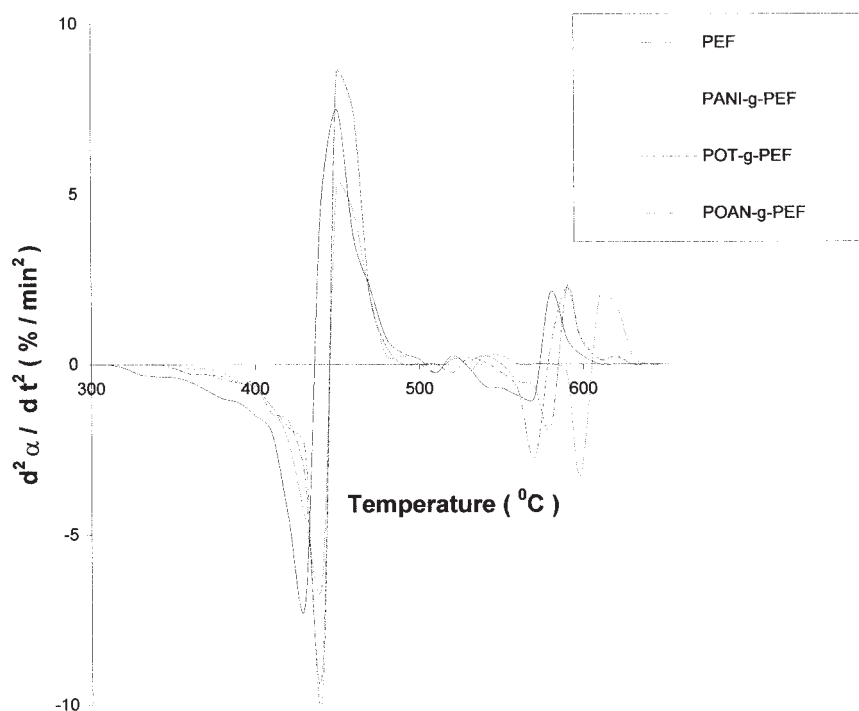

Figure 5 Friedman method $[-\ln(d\alpha/dt)$ vs $1/T]$ for the calculation of the activation energy of the thermal degradation of grafted and nongrafted substrates for the first major weight-loss step (300–500°C).

Figure 7 2DTG of the thermal degradation of grafted and nongrafted substrates.

and 500°C, may be attributed to the decomposition of the polyester backbone. The final weight-loss step (ca. 10–12%) was between 500 and 620°C. The weight-loss percentage in each weight-loss step and the char-residue percentage at 700°C are summarized in Table III. The weight-loss percentage for the major weight-loss step between 300 and 490°C was significantly higher for the parent nongrafted fabric (85.75%) than for the grafted substrates (ca. 70–75%). This indicates the higher thermal stability of the grafted substrates. Also, the char residue left at 700°C increased for all the grafted polyester fabrics in comparison with that of the parent nongrafted fabric, and it was highest for PANI-*g*-PET. This indicates that the grafted polyester fabrics had flame retardancy. Flame retardants have the ability to increase the conversion of polymeric materials into a char residue during pyrolysis and thus reduce the formation of flammable carbon-containing gases. The char helps to protect the substrate by interfering with the access of oxygen and induces flame retardancy.

DTG

Figure 4 shows the DTG thermogram curves of the grafted and parent nongrafted polyester substrates. The decomposition temperature data for the grafted and nongrafted substrates obtained from the DTG curves are summarized in Table IV. The temperature for the maximum weight loss for the two major weight-loss steps was higher for the grafted substrates

than for the nongrafted substrates. This again indicates the higher thermal stability of the grafted substrates in comparison with that of the parent nongrafted substrates. In case of the grafted substrates, POT-*g*-PET and POAN-*g*-PET were thermally less stable than PANI-*g*-PET because of the presence of a large number of methyl and methoxy groups, respectively, that could be easily excluded at an elevated temperature.

Degradation kinetics

The kinetic parameters of the thermal degradation for the grafted and nongrafted PET substrates were calculated[17] on the basis of Figures 5 and 6 by the Friedman technique with the following equation:

$$ln(d\alpha/dt) = lnZ + n \, ln(1 - \alpha) - E/RT$$

They were also calculated on the basis of Figure 7 by the Kissinger technique[18] with the following equation:

$$n = 1.88S \, (\text{for } S \geq 0.45)$$

$$S = |(d^2\alpha/dt^2)_{Lmax}|/|(d^2\alpha/dt^2)_{Rmax}|$$

where E is the activation energy; n is the decomposition reaction order; Z is the frequency factor of decomposition; $d\alpha/dt$ is the weight-loss rate obtained from the DTG curve; $1 - \alpha$ is the residual weight of the sample at a certain temperature obtained from the
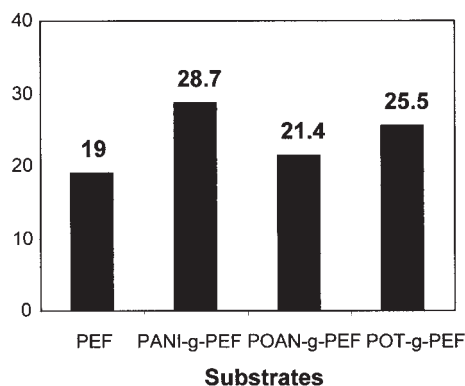
Figure 8   LOI values of PET, PANI-*g*-PET, POAN-*g*-PET, and POT-*g*-PET.

thermogravimetric curve; R and T are the gas constant and absolute temperature, respectively; and $(d^2\alpha/dt^2)_{L\ max}$ and $(d^2\alpha/dt^2)_{R\ max}$ are the two maximal $d^2\alpha/dt^2$ values at the left negative peak and right positive peak on the 2DTG curve at a single heating rate, respectively. As indicated in Table I, E and n for the thermal degradation steps are significantly higher for the grafted substrates (highest for PANI-*g*-PET) than for the nongrafted substrates. This indicates that the thermal stability of the PET substrate increased because of the grafting process.

Flame retardancy

The TGA data in Table III show that the grafted PET substrates had flame retardancy, which was evident from the increase in the char residue left at 700°C. This fact was confirmed by the LOI value, a measure of the induced flame retardancy. Figure 8 shows the LOI values of the grafted and parent nongrafted fabric substrates. The polyester fabrics grafted with PANIs showed flame retardancy, which was evident from the

increase in the LOI values of the grafted fabric substrates.

CONCLUSIONS

The grafting of PANIs [PANI, POAN, and POT] onto polyester fabric substrates improves the thermal stability of the substrates. Furthermore, these grafted substrates exhibit flame retardancy. At present, the use of these grafted substrates for the control of EMI and ESD is being explored.

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