Thermal Stability of Radiation-Grafted and Dyed Poly(ethylene terephthalate) Fabric

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ABSTRACT: The effect of degree of grafting (GY) and degree of dye uptake on the thermal stability of polyethylene terephthalate (PET) fabric was studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray diffraction analysis (XDA). TGA showed that the degradation process was composed of three overlapping stages. The first and second stages were studied in detail. Methacrylic acid (MAA)-grafted PET fabric was dyed using Rhodamine Red (RR) and Astrazonrot Violet (AV) basic dyes. It was found that grafting deteriorated the thermal stability of both stages. The first stage showed the formation of two new steps at low and high temperatures. Both steps are heating rate and graft yield dependent. The deteriorating effect of grafting was followed by the changes in the kinetic parameters. AV dyeing of grafted samples accelerated the degradation of both stages whereas RR dyeing improved the thermal stability to reach that of ungrafted fabric. XDA showed that the crystalline nature of AV dye stuff is responsible for the rapid degradation in both stages via the introduction of highly incompatible crystalline phase in the polymer back bone, which resulted in the formation of internal stresses that enhanced the degradation process. DSC measurements supported TGA results. The improvement in the thermal stability by RR dyeing is attributed to the amorphous nature and the high thermal stability of the RR dye stuff. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1007–1020, 2006

Key words: thermal stability; grafting; methacrylic acid; polyethylene terephthalate (PET); dyeing; kinetics; X-ray

INTRODUCTION

Because of the rigid structure, well-developed crystallinity, high hydrophobic properties, and lack of reactive dye sites, polyethylene terephthalate (PET) requires modification of its properties. Modification of the properties of PET fiber is usually carried out by radiation grafting with ionizing radiation.[1–10] Modification of the hydrophobic properties and the dyeability of polyester fabrics via radiation grafting with hydrophilic monomers have been carried out in our previous investigations.[1–3] The dyeability of methacrylic acid (MAA)-grafted PET fabric towards Rhodamine Red (RR) and Astrazonrot Violet (AV) (basic dyes) was improved significantly,[3] and low-temperature dyeing kinetics has been studied.[11] It was observed that the thermal properties of PET, measured by thermogravimetric analysis (TGA), were affected differently according to the treatment conditions of the fabric.[3]

Radiation grafting with ionizing radiation is expected to affect the properties of PET fibers. The effect of γ-radiation dose on the thermal degradation of PET fabric was studied in a previous investigation.[12] The degradation of the second stage followed a second-order kinetics and was independent of radiation dose or heating rate. The apparent activation energy of the degradation process and the logarithm of the pre-exponential rate constant have been affected considerably by increasing the radiation dose, and this was explained by structural changes in the matrix of PET fabric.

Radiation grafting of various phosphorus- and bromine-containing vinyl monomers onto polyester, cotton, and their blends was studied by Stannett et al.,[13] Liepins et al.,[14] and Zahran et al.[15] to impart flame-resistant and flame-proofing characteristics. The graft yield was enhanced by mutual peroxide and preirradiation method. Addition of 10% styrene to 2,3-dibromopropylacrylate (DBPA) was found to avoid rapid and complete homopolymerization, whereas addition of 10% MAA gave good grafting yields.[8] Similar investigations on grafting flame retardants onto PET/cotton blends by electron beam-induced grafting were reported by other investigators[16–18] to overcome the difficulty in obtaining reasonable graft yield. Nor[19] reported that according to differential scanning calorimetry (DSC) measurements the melting temperature of grafted PET fibers decreased slightly as the percentage grafting increases. Grafting and dyeing grafted

PET fabric to modify the physical, thermal, and the dyeing properties are expected to affect the glass-transition temperature as well as the high temperature stability. This article reports studies on the effects of degree of grafting of MAA onto PET and the degree of dye uptake of AV and RR (basic dyes), on the thermal degradation process. The study is based on the experimental results of TGA, DSC, and X-ray diffraction analysis (XDA). Changes in the thermal properties due to grafting and dyeing are followed by measuring changes in the structure of the fabric as well as changes in the kinetic parameters [reaction order (n), rate of conversion (R_C), rate constant (k_C), pre-exponential rate constant (A), and the apparent activation energy (Q)].

EXPERIMENTAL

Materials

Thermally stabilized (heat treated at 493 K for 1.5 min) low-density polyester fabric (product of Hancock Synthetic Inc., Korea) is mill-scoured in a solution containing 0.001 g/L Data scour WS-100 and sodium carbonate (0.5 g/L) at boiling for 1 h. The fabric was thoroughly washed with hot water, dried at ambient temperature, and then used for grafting.

The MAA monomer and other chemical reagents were used as-received. AV (CI 48,020) and RR (CI 45,170), basic dyes produced by Sandoz (Basle, Switzerland), were used.

Methods

Radiation grafting

Grafting was carried out by the direct irradiation method in a [60]Co γ source at a dose rate of 1.98 Gy/s with different doses and MAA concentrations to achieve a wide range of GYs. Dry and weighed PET samples (~0.7 g) were swollen in chloroform overnight before being put in wide-mouthed tubes with ground-glass stoppers. Also put in into each tube were methanol, the monomer, and 3 wt % grafting solution chloroform,[3] so that the fabric-to-liquor ratio was 1:40. The polyester solution was deaerated with bubbling nitrogen for 5 min. The grafted fabrics were removed from the reaction tube after irradiation to the desired dose. The homopolymer was extracted from the grafted fabrics with boiling water. The samples were then dried at 313 K in a vacuum oven to a constant weight. The degree of grafting was determined as the percentage increase in the weight.[2]

Dyeing procedure and CD measurements

Dyeing of PET fabric was carried out using AV and RR dyes. The structure of the dyes and dyeing procedure are given elsewhere.[3] Dyeing solutions were adjusted to 9.5×10^{-4} mol/L at predetermined pH. The dyeing process was carried out in the presence of 2% of weight of solution (ows) sodium sulfate and few drops of 0.1 g/L Sandozin NIT liquid (Sandoz), a wetting agent. The temperature of the dye bath was then raised to 360 K and kept constant for 45 min. After the dyeing, the samples were rinsed in hot water containing a nonionic detergent and in tap water and were allowed to dry. A computerized microcolorimeter unit was used to measure the color difference (CD) of dyed fabrics.[3] The CD was found to increase suddenly with the increase in graft yield up to 10% with a tendency to level off at higher degrees of grafting.

Apparatus

TGA studies were carried out on a Shimadzu TGA-30 apparatus (Shimadzu, Kyoto, Japan) at heating rates of 5 and 30°C/min in a nitrogen atmosphere over a temperature range from room temperature to 873 K. The primary TGA thermograms were used to determine the effect of different treatments on the thermal stability of PET samples. The primary thermograms conducted at 5 and 30°C/min heating rates were used to determine different kinetic parameters.

The degree of conversion and weight percent remain of the sample are calculated as follows:

$$\text{Degree of conversion (\%)} = 100[(W_o - W_T)/W_o] \quad (1)$$

$$\text{Remainder of sample (\%)} = 100(W_T/W_o) \quad (2)$$

where W_o and W_T are the weights of the original and heated samples, respectively. The weight fraction converted (C) or remained ($1 - C$) is the same as given in eqs. (1) and (2) without the percent.

DSC studies were performed using a Perkin–Elmer DSC-7 calorimeter (Perkin–Elmer Cetus Instruments, Norwalk, CT). A heating rate of 10°C/min was used under a nitrogen atmosphere.

XDA was performed using Shimadzu DP-DI with Cu Kα characteristic radiation.

RESULTS AND DISCUSSION

In a previous investigation,[12] we have shown that the thermal decomposition of polymers (R_C) is expressed by the equation

$$(R_C) = dC/dt = k_C(1 - C)^n \quad (3)$$

where dC/dt, C, k_C, and n are the rate of conversion, the conversion, the reaction rate constant, and the reaction order, respectively. The weight remaining (1
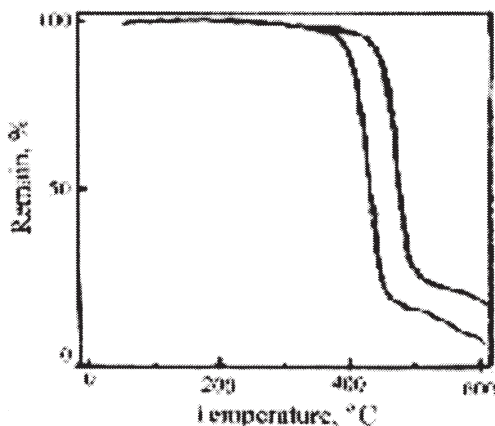
Figure 1 Representative TGA thermograms for ungrafted PET fabric at the heating rates 5 and 30°C/min.

$-$ C) is expressed as a fraction in this work. The rate constant k_C is temperature dependent and follows the Arrhenius-type rate equation

$$k = Ae^{-Q/RT} \qquad (4)$$

where A, Q, R, and T are the pre-exponential rate factor, the activation energy, the universal gas constant, and the absolute temperature, respectively. If the heating rate (dT/dt) of the sample is defined β then dC/dt can be rewritten as β (dC/dT).

The kinetic parameters were calculated by plotting the logarithm of dC/dt *versus* the logarithm of $(1 - C)$. The relationship is linear. Since the values of C and $(1 - C)$ are fractions and the rate of conversion decreases with the increase in the fraction remaining, the values of the slope n and log k of the straight line relationship are negative in sign. Both values, n and log k, are obtained from the equation displayed on the computer's chart. The activation energy of the decomposition and degradation processes are calculated from the values of the rate constants by carrying out the experiment at two different heating rates β_1 and β_2. On the basis of the displacement of the thermogravimetric curve due to the increase in heating rate, several methods have been used to calculate the value of Q. By comparing two thermograms with different heating rates, it can be deduced from eq. (4) that

$$Q(\text{J}/\text{mol}) = 19.04 T_1 T_2 (T_2 - T_1)^{-1} \log(k_2/k_1) \quad (5)$$

where, T_1 and T_2 are the absolute temperatures at the same degree of conversion for heating rates β_1 and β_2, respectively. The value of log (k_2/k_1) is obtained from the difference between the logarithms of k_2 and k_1 displayed on the computer's chart while the value of the pre-exponential rate constant A is calculated from the equation

$$\log A = \log k_C + Q/(2.3RT) \qquad (6)$$

In most TGA thermograms the rate of conversion of the second stage of the degradation process is the highest between 40 and 50% conversion. The temperatures corresponding to 50% conversion ($T_{50\%}$) are usually taken to calculate Q although other temperatures corresponding to constant conversion between 10 and 50% can as well be used. Deviations in the value of Q were noticed at 10 and 20% conversions.

Thermogravimetric analysis of PET fabric

Representative TGA thermograms for untreated PET fabric are shown in Figure 1 for the nominal heating rates 5 and 30°C/min. The general features of the percentage remaining weights as a function of temperature are the same except that the curves shift to the right (higher temperature) with the increase in the heating rate. The thermograms show three overlapping degradation processes. The first process occurs from room temperature to about 673 K and is a very slow degradation process. The second process is extremely fast, with a transition above 673 K, and occurs within 0.1–0.8 weight fraction converted. The third stage takes place at around 0.86 and 0.92 fraction converted, after which complete decomposition of the fabric occurs.

The values of the rates of conversion (dC/dt) of the second stage were calculated from the thermograms by multiplying the value of dC/dT, the slope of the fraction weight remaining by the value of the corresponding heating rate. The logarithm of conversion [log(dC/dt)] is then plotted as a function of the logarithm of the fraction remaining [log(1 − C)], according to eq. (3). Figure 2 shows the linear relationship between the logarithm of rate of conversion R_C (fraction converted/min) of the second stage and the logarithm of the fraction remaining (1 − C) for the 5 and 30°C/
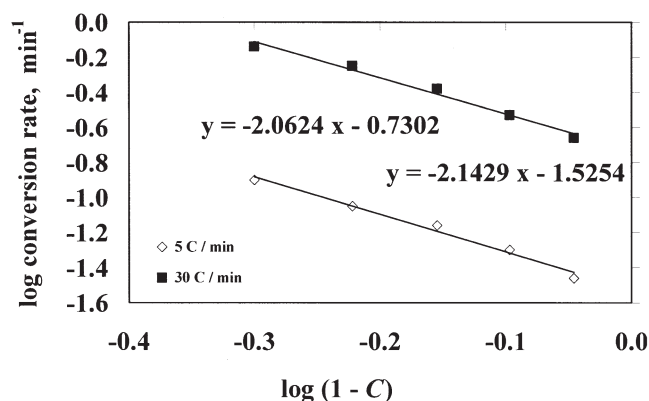

Figure 2 Logarithmic plots of the conversion rate R_C and weight fraction remain for ungrafted samples at the heating rates 5 and 30°C/min.

min heating rates. The relationship is linear and follows the equation

$$(\log R_C)_{30°C/min} = -2.0624\log(1 - C) - 0.7302 \quad (7)$$

$$(\log R_C)_{5°C/min} = -2.1429\log(1 - C) - 1.5254 \quad (8)$$

According to the section of kinetic analysis, the reaction order n is constant and is almost independent of the heating rate, and the degradation process follows a second-order kinetics. The intercepts of the equations give the values of -0.7302 and -1.5254 for $\log k_C$ for the heating rates 30 and 5°C/min, respectively. Inserting the values of $\log k_C$ in eq. (5) gives activation energy 244 kJ/mol for the second stage of untreated PET fabric. Substituting the values of Q, R_C, $T_{50\%}$, and $\log k_C$ in eq. (6) for the different heating rates give the value of $\log A$. An average value of 14.46 (min^{-1}) is calculated for $\log A$ for ungrafted PET fabric.

Effect of grafting on TGA thermograms

The effect of grafting on the TGA thermograms is shown in Figures 3(a) and 3(b) for 12.7 and 28% MAA-grafted PET fabric. The thermograms show that grafting significantly affected the first and second stage of the degradation process by changing the smooth and slow decrease in the degree of conversion of the first stage and the shift in the temperatures of the second stage to lower values (Fig. 1). This effect becomes significant for samples heated at the rate of 5°C/min. Details of the first and second stages are described here.

First stage of degradation

Two new degradation steps were formed in the smooth and slow degradation of the first stage and are graft yield and heating rate dependent [Figs. 3(a) and 3(b)]. For the heating rate of 5°C/min, the first step appears in the temperature range 328–383 K, whereas the second step starts about 473 K [Fig. 3(b)]. The first step is not observed clearly for samples grafted at 12.7% whereas 28%-grafted samples show both steps. The magnitude of the degree of conversion in this stage increases with increase in grafting. The total conversion of both steps amounts only to a few percent.

The effect of grafting on the degradation of both steps is followed by measuring the kinetic parameters and degree of conversion. The apparent activation energy for the both steps of the first stage of degradation is calculated from the simplified equation given by Ozawa.[20] This equation is similar to that of eq. (5) except that the rate constant k_{C1} and k_{C2} are replaced
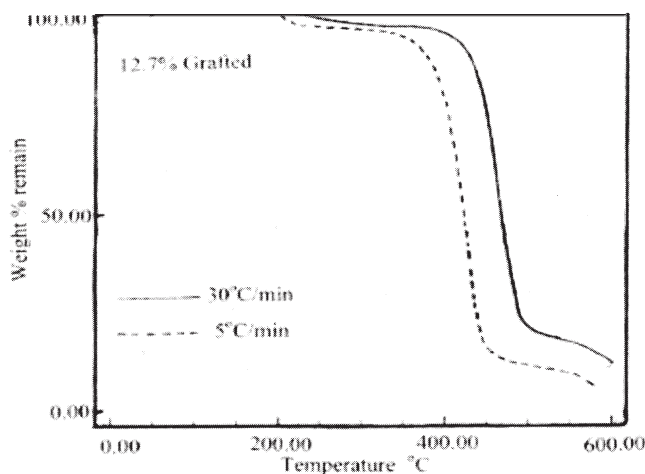

(a)
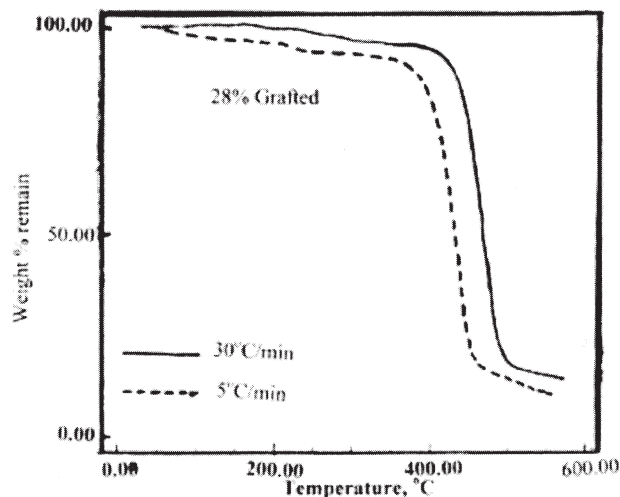
(b)

Figure 3 TGA thermograms for 12.7 (a) and 28%-grafted (b) PET fabric at the heating rates 5 and 30°C/min.

by the heating rates. The log (k_{C2}/k_{C1}) value becomes constant and equals to 0.778. An activation energy of 26 kJ/mol is calculated for the first step. The Q of the second step decreased from 73–47 kJ/mol as the GY increased from 12.7 to 28%. Moreover, the degree of conversion of the second step, measured at 648 K and the heating rate 5°C/min, increased linearly with the increase in GY at a rate of 0.405% GY^{-1} (Fig. 10).

The formation of the first and second degradation steps due to grafting can be attributed to the increase in the occluded water in the fabric due to the introduction of the hydrophilic carboxylic groups, which increases with the increase in graft yield.[3] An activation energy of 26 kJ/mol is required to evaporate the absorbed water in the fabric. The decrease in Q of the second step from 73 to 47 kJ/mol and the increase in conversion with the increase in the GY are due to the decomposition of the MAA copolymer, which increases with increase in GY.

(a)

(b)
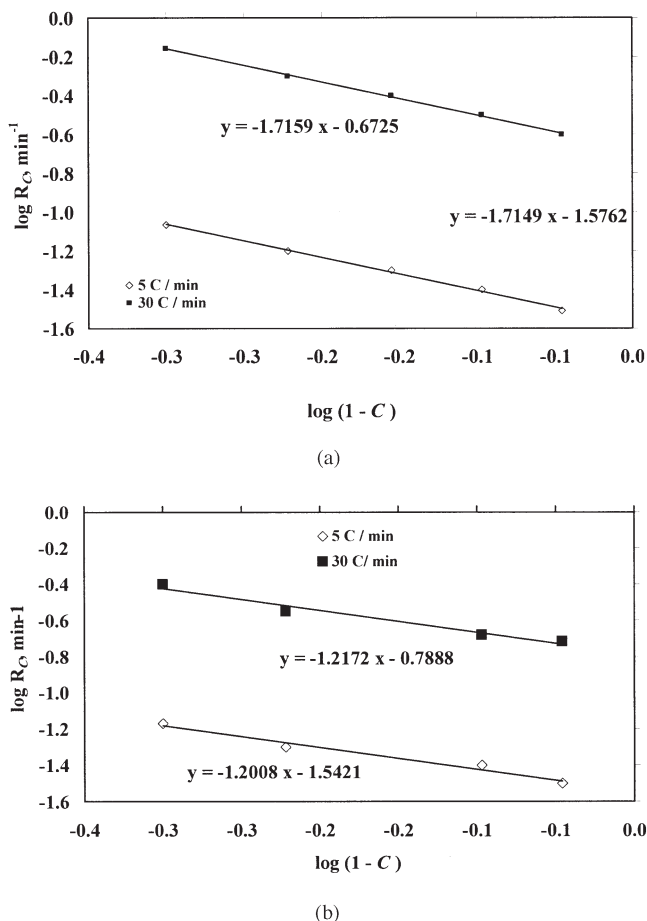
Figure 4 Logarithmic plots of the conversion rate R_C and weight fraction remain for 12.7 (a) and 28%-grafted (b) samples at the heating rates 5 and 30°C/min.

Second stage of degradation

The effect of grafting on the second degradation stage is shown in Figures 1 and 3. At a constant heating rate, the temperature corresponding to 50% conversion ($T_{50\%}$) of grafted samples is lower than that of ungrafted fabric. This effect becomes obvious from the study of the effect of heating rates on the characteristics of the TGA thermograms. Logarithmic plots of the conversion rates *versus* weight fraction remaining for the 12.7 and 28.0% PET-*g*-PMAA are shown in Figures 4(a) and 4(b). The linearity of the relationship is presented by the following equations.

For 12.7% grafts

$$(\log R_C)_{30°C/min} = -1.716 \log(1 - C) - 0.6725, \quad (9)$$

$$(\log R_C)_{5°C/min} = -1.715 \log(1 - C) - 1.5762, \quad (10)$$

For 28% grafts

$$(\log R_C)_{30°C/min} = -1.217 \log(1 - C) - 0.7888, \quad (11)$$

$$(\log R_C)_{5°C/min} = -1.201 \log(1 - C) - 1.5421, \quad (12)$$

Equations (9–12) indicate that the value of the reaction order n is independent of the heating rate but depends on the degree of grafting. It decreased with the increase in degree of grafting. Its value decreased from 2.1 for ungrafted fabric to 1.72 and 1.21 for 12.7 and 28%-grafted samples, respectively (Fig. 5). Figure 5 shows a linear decrease in n with the increase in GY according to the equation

$$n = -0.0318(GY\%) + 2.1068 \quad (13)$$

The reaction order decreased at 0.0318 as the GY increased by 1%. The intercept gives a value of 2.1068 to the order of degradation of ungrafted fabric.

The values of Q and $\log A$ are calculated from the intercepts of eqs. (7–12). Using eq. (5) and substituting the appropriate values of $T_{50\%}$ and $\log k_C$, average activation energies of 195 and 169 kJ/mol are calculated for the 12.7 and 28% grafts, respectively. Similarly, from eq. (6), average values of 13.2 and 11.2 (min^{-1}) are calculated for $\log A$ of 12.7 and 28%-grafted PET fabrics, respectively. The dependence of Q and $\log A$ on the degree of grafting is shown in Figure 6. The relationships show linear decrease of both independent variables with an increase in the GY, according to the following equations:

$$Q(kJ/mol) = -2.6455(GY\%) + 239(kJ/mol) \quad (14)$$

$$\log A(min^{-1}) = -0.1169(GY\%) + 14.53(min^{-1}) \quad (15)$$

Equations (14) and (15) indicate that the values of Q and $\log A$ decrease linearly with an increase in GY at 2.65 kJ/mol and 0.117, as the GY increases by 1%. The intercept of the straight lines with the *y*-axis at zero GY give values of 239 kJ/mol and 14.53 min^{-1} for Q and $\log A$, respectively, for the ungrafted PET fabric.
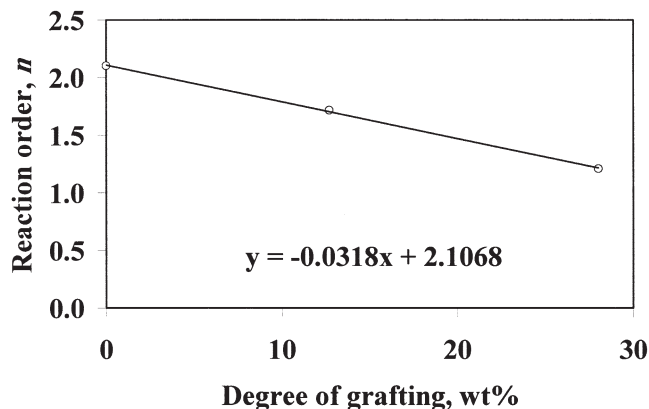
Figure 5 Dependence of reaction order on the degree of grafting.

(log A) = -0.1169 (GY)+ 14.539

Q = -2.65 (GY) + 239
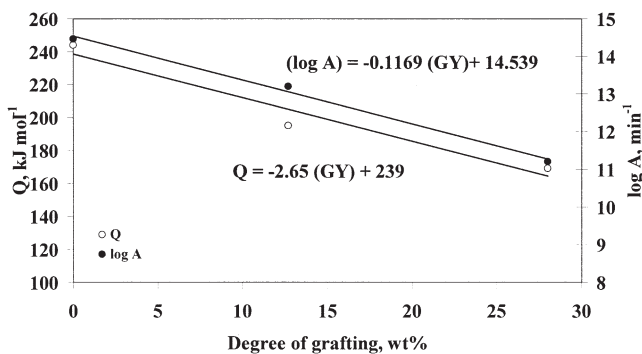
Figure 6 Dependence of the apparent activation energy Q and the pre-exponential rate constant log A on the degree of grafting.

Table I presents a summary of the effect of grafting on the kinetic parameters of the second stage of the degradation process.

The results given indicate that the mechanism of the second stage of the degradation process changes with the increase in graft yield. The energy required to decompose the back bone of the grafted fabric decreases with increase in degree of grafting. Moreover, for a constant value of the rate constant k_C, the rate of conversion R_C increases with the decrease in n, i.e., increase in GY. This increase in R_C with increase in GY is in consistence with the decrease in Q and log A with increase in grafting and indicates enhanced degradation with increase in GY. The effect of grafting on the degradation of the second stage can be attributed to the swelling effects resulting from the impregnation of samples in chloroform and the introduction of MAA copolymer in the matrix of PET fiber. The magnitude of swelling increases with the increase in GY. Moreover, grafting PET with MAA decreases the binding energy of PET by decreasing the bond energy. Similar results were reported by Sundardi et al.[21] during the study of the thermal stability of PET-AA (21.5%-grafted) fiber. They applied the analytical methods given by Reich[22] and Ozawa.[20] The results indicated similar decrease in activation energy with grafting. Table II shows a comparative study with our work according to the theoretical analysis given above. It is clear that Q values are higher than the values reported by Sundardi et al. This was attributed to different sample treatments.[12] Grafting PET with AA and MAA resulted in a decrease in the value of Q. The value of

the reaction order varies according to the fiber history,[5] degree and type of grafting monomer as well as the method of analysis.

Effect of grafting on DSC thermograms

Grafting PET samples with MAA changed the characteristic parameters of the DSC thermograms, mainly the glass-transition (T_g) and melting (T_m) temperatures as well as the corresponding heats of transition. DSC is carried out to explain the changes observed in the first stage of TGA thermograms. Figure 7 shows representative DSC thermograms for 12.7%-grafted and ungrafted samples carried out at 10°C/min heating rate. The endothermic peaks at T_g started to appear by grafting and the temperature decreased from 80°C[12] to around 65°C with grafting. No observable change in T_g is noticed, as the degree of grafting increases from 7.9 to 12.7%. Moreover, grafting showed no effect on the value of T_m, and it remained constant at 259°C. The temperature range of softening the fibers increased with grafting and the heats of glass transition and fusion (ΔH_g and ΔH_f) changed with grafting. The value of ΔH_g increases considerably from 9.76 to 48.4 kJ/kg with the increase in GY from 12.7 to 28%. The heat of fusion ΔH_f behaved oppositely. For the same changes in degree of grafting, ΔH_f decreased from 32.3 to 17.8 kJ/kg, with the increase in GY from 12.7 to 28%. A summary for the effect of grafting on DSC parameters is given in Table III. It is clear from Table III that the values of T_g and ΔH_g can be considered as a measure of the degree of crystallinity and stability of PET fabrics especially for the first stage of the degradation process. As the value of T_g decreases and ΔH_g increases, the degree of thermal stability decreases. The value of T_m is constant (259°C) and is independent of the degree of grafting The heat of fusion of grafted fabric, however, does not deviate from that of ungrafted one (around 31 kJ/kg) up to 12.7% GY. Further increase in the degree of grafting to 28% resulted in a decrease in ΔH_f to 17.8 kJ/kg. This indicated a change in the degree of crystallinity of the fabric. The heats of glass transition and fusion are considered to be qualitative, since the molecular weights of ungrafted and grafted PET fabrics are unknown.

DSC results support the decrease in the degree of crystallinity of PET fabric due to grafting. Consequently, the binding energy of PET-g-PMAA is ex-

TABLE I
Kinetic Parameters of the Second Stage for Grafted and Ungrafted PET Fabric

Fiber	Reaction order	log k_C at 30°C/min	log k_C at 5°C/min	Q (kJ/mol)	log A (min^{-1})
Ungrafted	2.1	−0.7302	−1.5254	244	14.46
12.7% graft	1.72	−0.5725	−1.5762	195	13.2
28% graft	1.21	−0.7888	−1.5421	169	11.2

TABLE II
Comparative Results with Other Authors on the Kinetic Parameters of Thermal Degradation of Grafted and Ungrafted PET Fibers

Fiber	Activation (kJ/mol)			Reaction order (n)	
	Reich[22]	*Qzawa*[10]	*This work*	*Sundardi*[21]	*This work*
PET (0%)	204,94 ± 6.77	204.74 ± 6.56	241 ± 2.6	1.30	2.10
PET-AA (21.5%)	177 ± 14.42	171.63 ± 15.88	—	2.27	
PET-MAA (12.7%)	—		195		1.72
PET-MAA (28%)	—		169		1.21

pected to be lower than that of untreated PET as given by the decrease in the kinetic parameters mentioned in TGA measurements.

Effect of dyeing on the TGA of grafted PET fabric

First stage

The effect of dyeing grafted PET samples with AV dye on the TGA thermograms is shown in Figure 8. Figure 8 shows thermograms for PET fabric grafted to 7.5 and 26% and dyed with AV dye. The thermograms for the heating rate 5°C/min show the disappearance of the first step and a considerably high degradation in the second step of the first stage. The degree of conversion of the second step (decomposition of MAA copolymer) increased by the increase in dye uptake (GY). The difference in conversion between grafted and dyed samples decreases with the increase in temperature tending to zero close to $T_{50\%}$, indicating the complete decomposition of MAA copolymer. The value of Q at 5% conversion decrease considerably with AV dye

uptake. It decreased from 63 to 35 kJ/mol as the graft yield (dye uptake) increased from 7.5 to 26% (Table IV).

Figure 9 shows thermograms of PET fabric grafted to 7.5% and 29.3% and dyed with RR dye. It is clear from the curves that the features of the thermograms for 7.5%-grafted and RR-dyed samples is the same as that of ungrafted one allover the temperature range with nearly the same value of $T_{50\%}$. Dyeing 29.3%-grafted PET samples with RR dye resulted in the start of the appearance of the first step.

The effect of GY (dye uptake) on the degree of conversion of the second step of the first stage of the degradation process for grafted, AV-dyed, and RR-dyed grafted samples measured at 648 K for the heating rate of 5°C/min is shown in Figure 10. The degree of conversion increased linearly with the increase in graft yield with slopes of 0.235, 0.405, and 1.388% GY^{-1} for RR-dyed, grafted, and AV-dyed samples, respectively. The slope of the relationship is a measure of the degree of degradation of the second step of the degradation process. Since the dye uptake increases with the increase in grafting,[2,11] the excessive deterioration (3.43 times that of grafting) and improvement (0.58 times that of grafting) in the stability of the fabric is due to the increase in AV and RR dye uptake and not to grafting.

The disappearance of the first step of samples dyed with both dyes at low and high GY can be explained by the decrease in the number of carboxylic groups introduced by grafting. The COOH groups react with the basic dyes to form $—COO^-—^+Dye$ bond. The reduction in the number of carboxylic groups will result in the decrease in water molecules absorbed by the dyed fabric. Since the first step is attributed to the
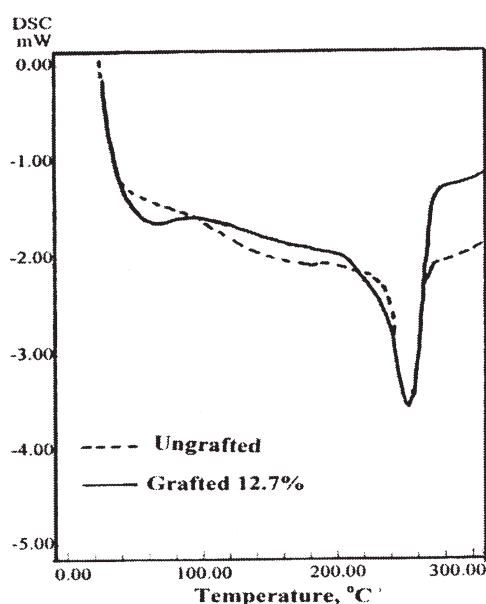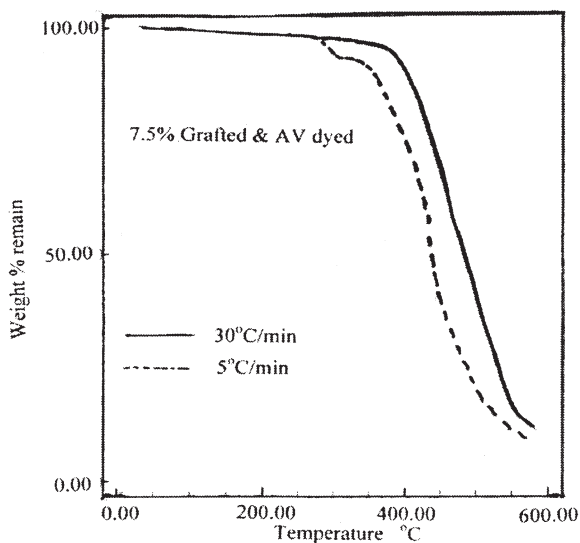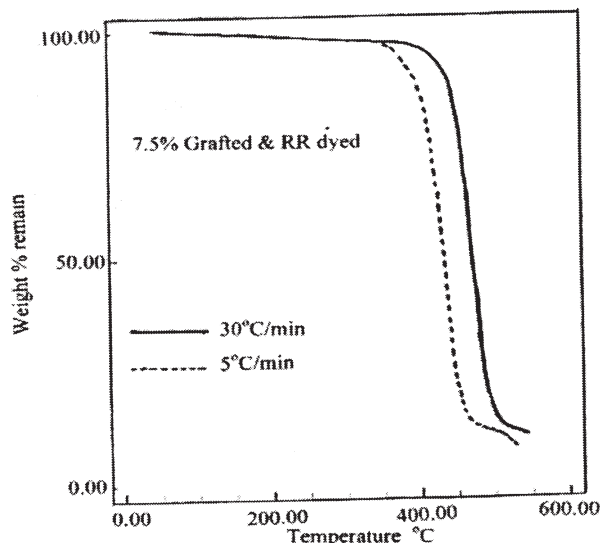

Figure 7 Representative DSC thermograms for ungrafted and 12.7%-grafted PET fabric at the heating rate 10°C/min.

TABLE III
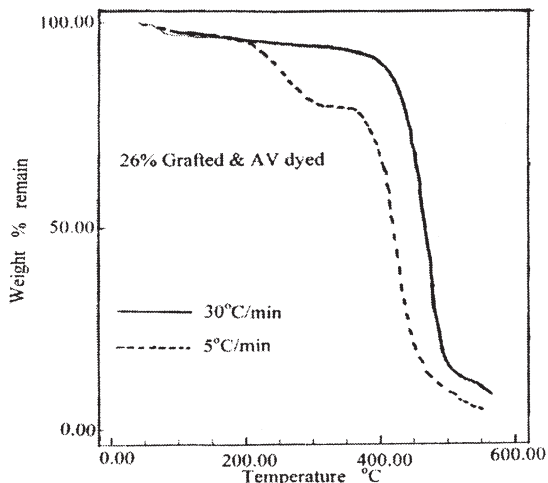**Effect of Grafting on DSC Parameters of PET Fabric**

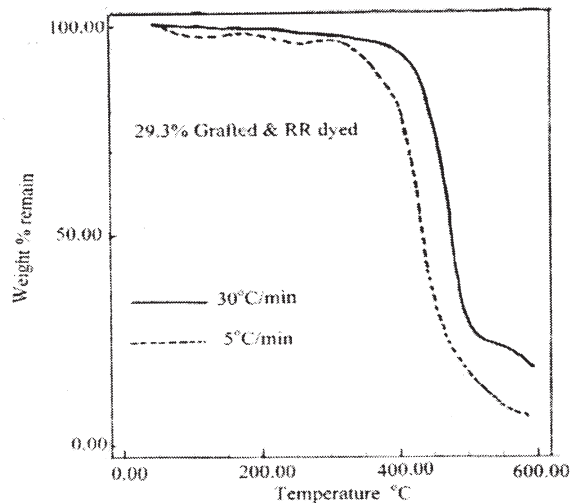| Treatment	T_g (°C)	T_m (°C)	ΔH_g (kJ/kg)	ΔH_f (kJ/kg)
Ungrafted	78.0	258.5	Undetected	31.4
7.9% graft	65.0	259.2	4.6	29.3
12.7% graft	65.6	259.4	9.7	32.4
28.0% graft	65.8	259.5	48.4	17.8

Figure 8 TGA thermograms for 7.5 (a) and 26%-grafted (b) and AV-dyed PET fabric.

Figure 9 TGA thermograms for 7.5 (a) and 29.3%-grafted (b) and RR-dyed PET fabric.

evaporation of water content during heating, the increase in dye uptake by the increase in grafting will result in the disappearance of the first step. Hence dyeing will decrease the hydrophilic properties of grafted fabrics.

Second stage

The logarithmic plots of the conversion rate versus the fraction remaining of AV-7.5%-grafted and AV-26%-grafted samples at the second stage of the degradation process are shown in Figures 11(a) and 11(b). The

TABLE IV
Dependence of the Activation Energy Q of the Second Step of the First Stage on the Graft Yield GY, Dye Content, and Type of Basic Dye

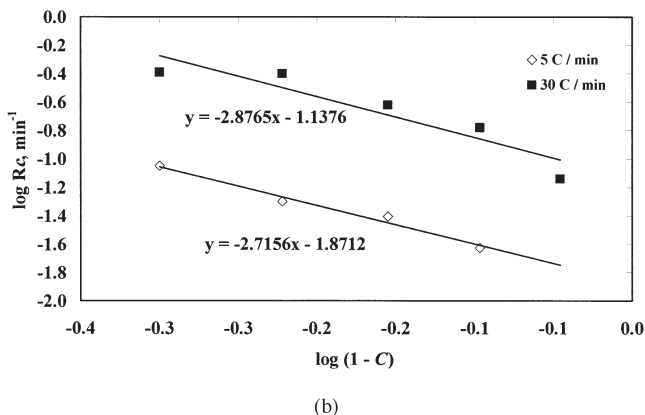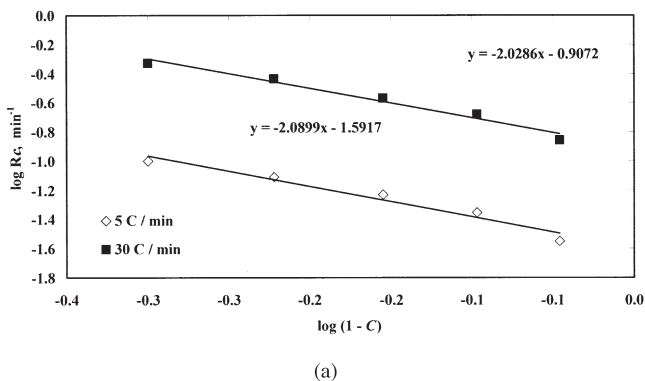| Fabric	12.7% grafted	28% grafted	AV		RR	
			(7.5% GY)	(26% GY)	(7.5% GY)	(29.3% GY)
Q (kJ/mol)	64.4 at 5% conversion	28.9 at 5% conversion	60.0 at 5% conversion	31.8 at 10% conversion	Undetected	35.8 at 2.5% conversion
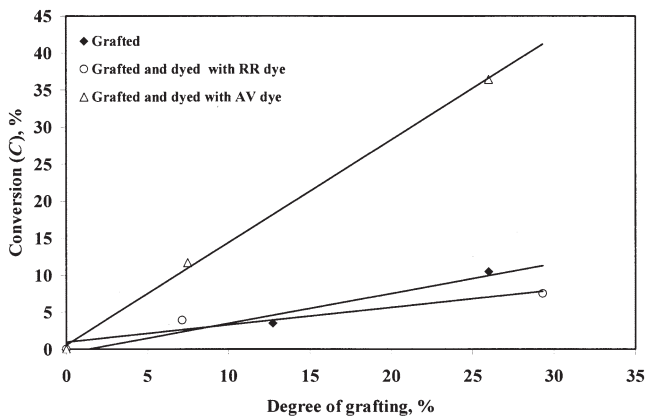
Figure 10 Dependence of degree of conversion at 648 K on the degree of grafting for samples heated at 5°C/min.

reaction order is almost constant (1.82) and is independent of the graft yield of the substrate. This implies that the reaction order is affected by dyeing and indicates the important role of the dye in the degradation process. The values of the intercepts of the straight line relationship between $\log R_C$ versus $\log (1 - C)$ are

Figure 12 Logarithmic plots of the conversion rate R_C and weight fraction remain for 7.5 (a) and 29.3%-grafted (b) and RR-dyed samples at the heating rates 5 and 30°C/min.

-1.0513 and -1.6854 for AV-7.5%-grafted samples heated at the rates 30 and 5°C/min, respectively. For the given heating rates, the corresponding values of $\log k_C$ for AV-26%-grafted fabric are -0.9520 and -1.8091. The calculated apparent activation energies are 160 and 165 kJ/mol for the AV-7.5%-grafted and AV-26%-grafted samples, respectively. However, AV dyeing of 7.5%-grafted samples resulted in a rapid decrease in Q of grafted PET from 220 (Fig. 6) to 160 kJ/mol, with no further decrease at higher degrees of uptake of AV dye.

Similar logarithmic plots for samples grafted to 7.5% and 29.3% and RR-dyed is shown in Figure 12. The results for grafted and AV- and RR-dyed samples are given in Table V. It is clear from Table V that the

Figure 11 Logarithmic plots of the conversion rate R_C and weight fraction remain for 7.5 (a) and 26%-grafted (b) and AV-dyed samples at the heating rates 5 and 30°C/min.

TABLE V
Kinetic Parameters for AV and RR-Dyed-Grafted Fabrics

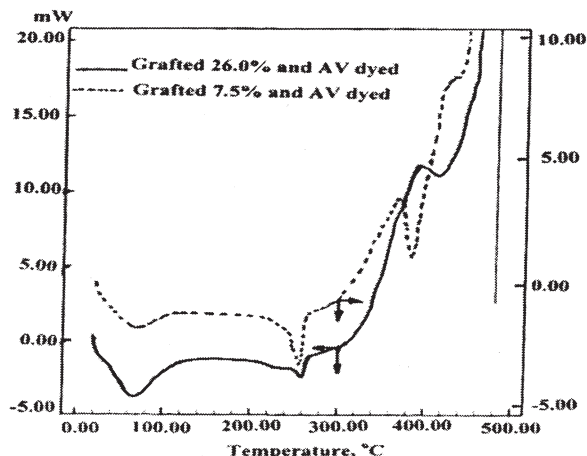| Fibre	Reaction order	$\log k_C$ at 30°C/min	$\log k_C$ at 5°C/min	Q (kJ/mol)	$\log A$ (min^{-1})
AV (7.5%)	1.8	-1.0513	-1.685	160	9.6
AV (26.0%)	1.8	-0.952	-1.809	165	10.8
RR (7.5%)	2.05	-0.907	-1.592	205.6	14.0
RR (29.3%)	2.79	-1.137	-1.871	229.7	15.1

Figure 13 DSC thermograms for grafted and AV-dyed PET fabric.

values of the reaction order of RR-dyed samples are higher than those of AV-dyed ones (1.82), which in turn are higher than those of grafted samples. The reaction order for RR-dyed 7.5%-grafted samples reached the value of ungrafted one (2.05) while RR-dyed (29.3%) samples show reaction order of 2.79. Moreover, the activation energy for the second stage of the degradation process of RR-dyed samples increases considerably with the increase in graft yield of the PET substrate, i.e., increase in dye content.[2,3] The value of Q increased from 206 to 230 kJ/mol, as the degree of grafting (or RR dye content) increases from 7.5 to 29.3%. The RR-dyed grafts, however, give values for log A that increase with the increase in graft yield or dye content. The values of log A for RR-dyed samples (14.04 and 15.12 min^{-1} for 7.5 and 29.3% grafts) are higher than those for grafted and even untreated samples (Table I).

DSC measurements were made to support the significant differences between AV- and RR-dyed grafted samples. Figures 13 and 14 show DSC thermograms for AV- and RR-dyed samples grafted to different degrees. The results given in Table VI show the values of the transition temperatures (T_g and T_m) and the corresponding heats of the processes (ΔH_g and ΔH_f) together with the heat of decomposition (ΔH_d) at temperatures of 653 and 693 K. The DSC parameters for grafted samples are included for comparison. The glass-transition temperature for differently treated samples falls around 338.5 K and increased suddenly to 353.2 K for 29.3%-grafted and RR-dyed fabric, reaching the value of ungrafted samples.[12] The regain of the value of T_g to that of untreated fabric indicates the increase in the degree of stability via RR dyeing of samples with high degrees of grafting. The values for T_m, however, stayed almost constant around 532.5 K. The heat of glass transition ΔH_g and that of fusion ΔH_f show different behavior. The heat of fusion for

grafted, grafted and AV- and RR-dyed samples show values around that of untreated sample and amounted to 32 kJ/kg, with lower values for 26%-grafted and 29.3%-grafted and RR-dyed fabric. The 26%-grafted and AV-dyed sample, however, showed the highest value of 41.9 kJ/kg for ΔH_f, indicating highest degree of disorder. The heat of glass transition for grafted, AV- and RR-dyed samples showed a considerable dependence on the degree of grafting. Figure 15 shows nearly binomial increase in ΔH_g with the increase in graft yield. This increase in ΔH_g with the increase in GY follows the following order: grafted and AV-dyed > grafted > grafted and RR-dyed samples. This order is exactly similar to that obtained from the dependence of the degree of conversion on the graft yield presented in Figure 10. This indicates that the thermal stability of grafted and RR-dyed samples is higher than those of grafted and grafted and AV-dyed samples.

The remarkable changes in the first stage and the kinetic parameters of the second stage of the degradation process due to dyeing grafted samples with AV and RR dyes emphasize the necessity for further understanding the different modifications in the grafted fabrics due to dyeing. These modifications are followed by investigating structural changes in the fabric due to dyeing and the thermal stability and structure of the dye stuff itself.

The thermal stability of the dye stuffs is carried out at the heating rate of 5°C/min. The TGA thermograms for the AV and RR dyestuffs are shown in Figure 16. It is clear from Figure 16 that the stability of RR dyestuff is higher than that of AV dye above 337°C ($T_{18.7\%}$). The temperature corresponding to 10% conversion is 482 and 557 K for AV and RR dyestuffs, respectively. The rate of conversion of RR dye is higher than that of AV
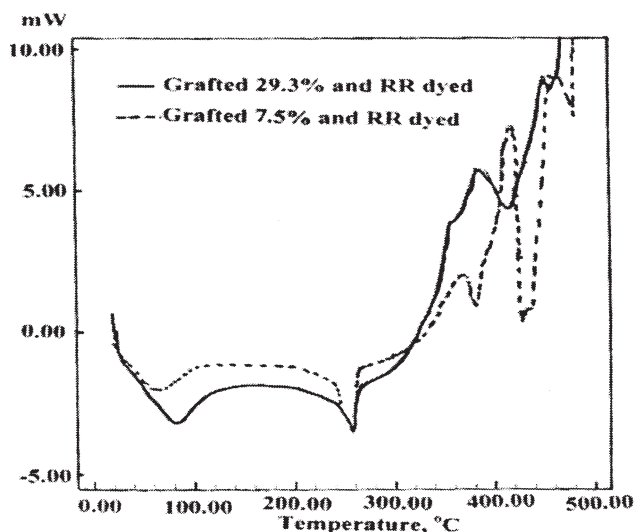

Figure 14 DSC thermograms for grafted and RR-dyed PET fabric.

TABLE VI
DSC Parameters for Grafted, AV, and RR-2 Dyed Grafted PET Fabric

Treatment	T_g (°C)	T_m (°C)	ΔH_g (kJ/kg)	ΔH_f (kJ/kg)	ΔH_d (kJ/kg) at T_d (°C)
7.9% graft	65.1	259.1	4.6	27.3	—
12.7% graft	65.5	259.4	9.8	43.2	—
26% graft	65.8	258.6	48.4	17.8	—
7.5% AV	66.0	260.0	15.9	35.2	27.9 at 380
26% AV	66.1	260.0	89.7	41.9	12.1 at 420
7.5% RR	66.0	255.5	4.8	33.5	15.1 at 380
29.3% RR	80.2	258.6	18.2	21.6	7.6 at 420

dye above $T_{18.7\%}$. The temperature corresponding to 50% conversion $T_{50\%}$ for RR dye is about 787 K whereas that for AV dye is higher than 873 K. The values of $T_{10\%}$ and $T_{50\%}$ for grafted PET fabric are around 673 and 693 K, respectively, and are GY dependent. Consequently, one would expect considerably high degrees of conversion in the first stage of the degradation process upon dyeing grafted samples with both dyes with a significantly high effect from AV dye. This explanation agrees, to a certain extent, to the results of the initial stage of the degradation process for grafted and AV- and RR-dyed samples. High degrees of grafting (26 and 29.3%) result in the increase in dye uptake, which shows itself in the increase in the degree of conversion and heat of fusion with the increase in GY (Figs. 8–10 and 15). This effect is not significant, since the dye uptake of grafted fabric is extremely small if compared with that of the dyestuff itself[2,3,11,23] (2–3 mg). Moreover, it is expected that both dyes should improve the high temperature stability (second stage) of grafted fabric with better results for AV dye, since its high temperature stability is better than RR dye and the untreated PET fabric itself. This is in contradiction with the calculated activation energies shown in Table V.

The aforementioned discussion does not clearly indicate the real factor that affects the thermal stability of AV- and RR-dyed grafted PET fabric. Therefore, one has to look for structural changes resulting from dyeing grafted fabrics. XDA of grafted, AV- and RR-dyed grafted samples were carried out to look for structural changes due to dyeing. Table VII shows the XRD parameters for the strongest three peaks of grafted, grafted to low and high yields and dyed with AV and RR dyes together with those for both dyestuffs. Figure 17 shows the diffraction patterns for 28%-grafted, 26%-grafted and AV-dyed, and 29.3%-grafted and RR-dyed samples. The results presented in Table VII and Figure 17 indicate the following: (1) The values of the diffraction peaks at 2θ angles and the corresponding lattice plane spacing (d) for grafted, grafted and RR-dyed samples, at low and high degrees of grafting, are nearly the same. This indicates that increase in the degree of grafting or dyeing grafted fabric with RR dye has little effect in the structure of grafted PET fabric; (2) Dyeing grafted fabric with AV dye shows two significant changes in the diffraction pattern of grafted fabric. The low-angle diffraction peaks resulting from the dyeing of grafted fabric at 7.5 and 26% GY (23.671, 24.350, and 26.559 2θ, and d values of 3.7556, 3.6523, and 3.3534 Å) are different from those of grafted and RR-dyed grafted samples and are independent of AV dye content (GY). The striking effect of AV dyeing of grafted samples is the
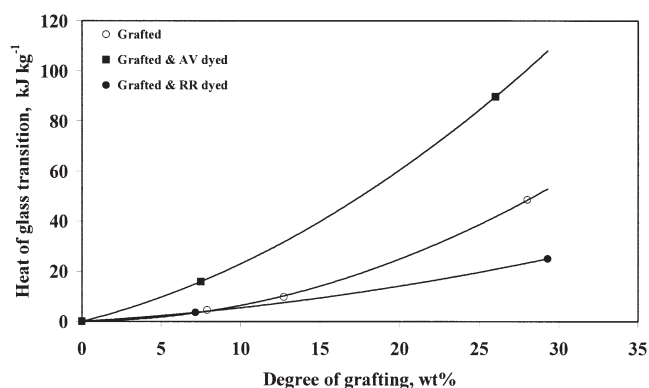

Figure 15 Dependence of heat of glass transition on the degree of grafting for differently treated samples.
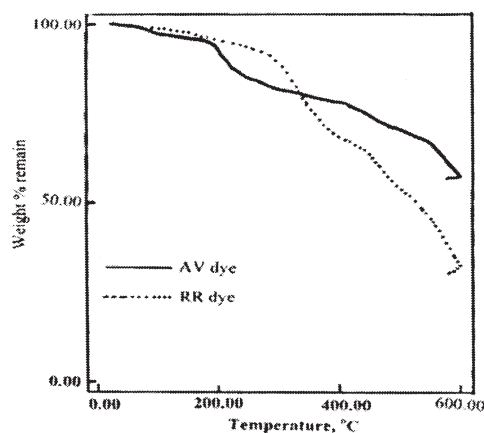

Figure 16 TGA thermograms for AV and RR dyestuffs at the heating rate of 5°C/min.

TABLE VII
X-Ray Diffraction Patterns for Grafted, Grafted and
Dyed, and AV and RR Dye Stuffs

Fabric	2θ (°)	d, (A)	I (cps)	I/I₁
28% grafted	14.618	6.0545	68	100
	16.318	5.4274	33	48
	21.078	4.2114	20	29
7.5% grafted and AV-dyed	24.350	3.6523	70	100
	26.559	3.3534	65	92
	23.671	3.7556	65	92
7.5% grafted and RR-dyed	25.709	3.4623	78	100
	16.536	5.3565	68	87
	22.821	3.8934	68	80
26% grafted and AV-dyed	64.102	1.4515	60	100
	77.353	1.2326	55	91
	44.056	2.0537	53	87
26% grafted and AV-dyed	26.549	3.2914	52	100
	23.841	3.7292	50	96
	24.690	3.6028	40	79
29.3% grafted and RR-dyed	16.998	5.2118	90	100
	14.108	6.2722	85	94
	20.908	4.2452	60	66
AV dyestuff	20.058	4.4232	443	100
	33.317	2.6870	378	85
	30.088	2.9677	250	56
RR dyestuff	Undetected	—	—	—

The table header column labeled *I* spans over (cps) and *I/I₁*.

appearance of well-defined and sharp peaks at the low- and high-angle sides of the diffraction pattern (Fig. 17). Broad peaks are located at the low-angle side and sharp well-defined peaks are located at 44.056, 64.102, and 77.353 2θ, and *d* values of 2.0537, 1.4515, and 1.2326 Å. The changes in the diffraction pattern of grafted PET fabric at low and high dye content (GY) show that the lattice spacing of grafted fabric decreases upon dyeing. The low-angle lattice spacing of AV-dyed grafted samples decreased, on the average, by 32% of that of grafted or RR-dyed samples. The newly formed peaks at the high-angle side of the diffraction pattern have diffraction spacing less by 68% than those of grafted samples. The observed remarkable changes in the low-angle diffraction pattern
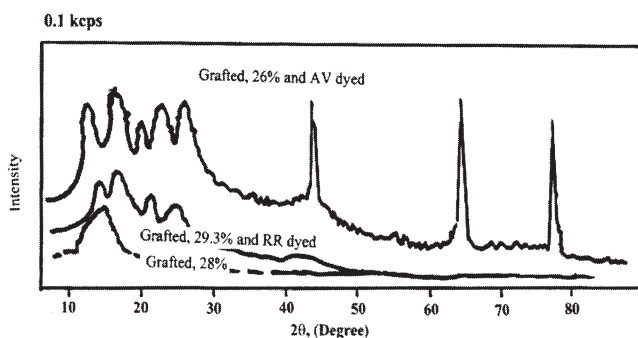

Figure 17   X-ray diffraction patterns for 28%-grafted, 26%-grafted and AV-dyed, and 29.3%-grafted and RR-dyed samples.
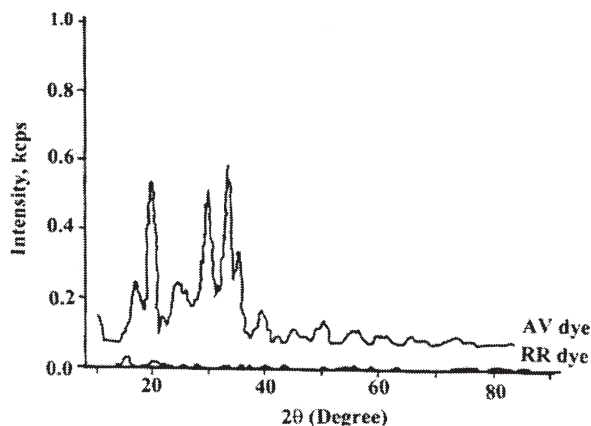

Figure 18   X-ray diffraction patterns for AV and RR dye-stuffs.

and the formation of the high-angle new peaks indicate that the introduction of AV dye into grafted PET samples results in the distortion of the structure as well as the formation of new crystal lattice in the matrix of highly grafted samples.

The discussion given above suggests the study of the diffraction patterns of the RR and AV dyestuffs. Figure 18 and Table VII shows the X-ray patterns for both dyestuffs. It is obvious that the structure of RR dye is completely amorphous while that of AV dye is highly crystalline. The strongest and distinctive three diffraction peaks for the AV dye is located at 20.058, 30.317, and 33.317 2θ, with *d* values of 4.4232, 2.9677, and 2.6870 Å. These parameters are, to a certain extent, close to those obtained for AV-dyed grafted samples (Table VII). This indicates that the introduction of the crystalline AV dye in the grafted regions (crystalline and amorphous regions of PET fabric) and the formation of a new structure, having lattice parameters different than those of grafted PET fabric results in the formation of internal stresses due to the lower degree of compatibility between them. These stresses accelerated the degradation rate of the second step due to grafting from 0.405 to 1.388%GY^{-1}, and resulted in the further decrease in the activation energy of grafted fabric with the increase in GY (dye uptake) to 7.5%. The apparent activation energy of AV-dyed samples can thus be presented as follows:

$$Q_{AV} = Q_{Gr} - Q_{st} \ (\text{J mol}^{-1})$$

where, Q_{AV}, Q_{Gr}, and Q_{st} are the activation energies of AV-dyed grafted sample, grafted sample, and that resulting from internal stresses. The value of Q_{st} equals σV, where σ and V are the internal stresses (N/m^2) and the volume per mole (m^3/mol) of the fibers matrix, respectively.

The RR dye, however, being completely amorphous, shows no effect in the structure of grafted

samples, since the peak angles and lattice spacing are almost the same for 28%-grafted samples and 29.3%-grafted and RR-dyed fabrics. The existence of the compatible and amorphous structure of RR dye with the high thermal stability in the amorphous regions of PET fabric results in the observed increase in the thermal stability of the grafted fabric. Moreover, the observed improvement in the first stage of the degradation process of RR-dyed samples is attributed to the decrease in the moisture content of grafted PET samples via dyeing with RR dye. The dyeing process results in a decrease in the hydrophilic (carboxylic) functional groups, and thus decreased the moisture content, which is responsible for the loss in the weight of samples, especially for those having high degrees of grafting.

CONCLUSIONS

The following conclusions were reached from the study of the effects of the degree of grafting MAA onto PET and the degree of dye uptake of AV and RR dyes on the first and second stages of the degradation process of untreated samples:

1. Grafting increased the degradation of the first stage of untreated fabric by the appearance of two new degradation steps that are heating rate and GY dependent. The steps appeared at the slow heating rate of 5°C/min and GY of 28% at temperatures of 328 and 473 K. The second step appeared only at high GY (28%). The degree of conversion of the second step at 648 K increased linearly with the increase in GY at a rate of 0.405% GY^{-1}, whereas the apparent activation energy Q, measured at 5% conversion, decreased from 73 to 45 kJ/mol with the increase in graft yield from 12.7 to 28%.

2. DSC measurements supported the deteriorating effect of grafting on the first stage by decreasing the degree of crystallinity of untreated samples. This conclusion is reached through the decrease in T_g from 353 to 339 K and increasing the heat of glass transition ΔH_g from 9.76 to 48.4 kJ/kg, as the degree of grafting increased from 12.7 to 28%, respectively.

3. The appearance of the first and second steps due to grafting is attributed to the removal of the excess water absorbed resulting from the introduction of the hydrophilic COOH groups in the fiber matrix and the start of the decomposition of MAA copolymer, respectively.

4. Grafting deteriorated severely the thermal stability of the second stage of the degradation process by shifting the $T_{50\%}$ to lower values and decreasing the kinetic parameters. The reaction order n, the apparent activation energy Q, and the logarithm of the pre-exponential rate constant log A decreased linearly at the rates of 0.0318 GY^{-1} order, 2.646 kJ/mol GY^{-1}, and 0.117 min^{-1} GY^{-1}, respectively, with intercepts of 2.10, 239 kJ/mol, and 14.54 min^{-1} for n, Q, and log A of untreated fabric. The deterioration of the second stage is attributed to the decrease in the PET bond energy resulting from the swelling effects of chloroform and MAA grafting.

5. Dyeing grafted fabric with AV dye deteriorated severely the thermal stability of the second step of the first stage of grafted PET fabric. The degree of conversion of the second step of grafted samples, measured at 648 K, increased from 0.405%GY^{-1} to the rate 1.388%GY^{-1} (3.43 times) with the increase in AV dye uptake whereas the Q, at 5% conversion, decreased from 63 to 35 kJ/mol with the increase in GY (dye uptake) from 7.5 to 26%. The degradation of MAA copolymer extended up to the second stage up to $T_{50\%}$.

6. AV dyeing of grafted fabric deteriorated the second stage of the degradation process by shifting the $T_{50\%}$ of grafted fabric to lower values and decreasing the Q and log A of 7.5%-grafted samples from 220 kJ/mol and 13.7 min^{-1} to 160 kJ/mol and 9.6 min^{-1}, with no further changes at higher AV dye uptake.

7. RR dyeing improved significantly the thermal stability of both stages of grafted fabric. The first step of the first stage resulting from grafting disappeared at 7.5% GY whereas the magnitude of conversion of the second step is lower that that of grafted or AV-dyed samples. The values of n, Q, and log A increased from 2.05 order, 205.6 kJ/mol, and 14.04 min^{-1} to 2.75 order, 2.79, to 229.7 kJ/mol, and to 15.12 min^{-1}, respectively, with the increase in graft yield from 7.5 to 29.3%. The improvement in the thermal stability of RR-dyed samples reached that of untreated fabric.

8. DSC measurements of RR-dyed PET supported the results of TGA and showed that the degree of crystallinity of the dyed fabric, as measured by the glass-transition temperature T_g, reached that of untreated fabric (353 K).

9. XDA of AV-dyed fabric revealed the formation of a highly crystalline phase in the crystalline and amorphous regions of grafted fabrics. This resulted in the formation of internal stresses that enhance the degradation process of both stages. The improvement in the thermal stability of the first step by AV and RR dyeing grafted samples is attributed to the decrease in number of carboxylic groups via their reaction with the basic dye molecules. The high thermal stability of the

RR-dyed samples is attributed to the amorphous nature and the high thermal stability of the RR dyestuff.

10. The degree of deterioration of the thermal stability of differently treated PET fabric follows the order: AV-dyed samples > grafted samples > RR-dyed samples ≥ untreated samples.

11. It is recommended to dye grafted samples with amorphous dyestuffs rather than those having crystalline structure, since the latter deteriorate drastically the thermal stability of PET fabrics.

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