Modification of polyester fabric via radiation grafting with methacrylic acid

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Received 23 December 2002; revised received 16 June 2003; accepted 17 September 2003

Polyester fabric has been modified by radiation graft copolymerization with methacrylic acid (MAA) to improve its hydrophilic, dyeing and thermal properties. It is observed that the efficiency of grafting significantly depends on swelling agent, solvent, monomer concentration and irradiation time. The initial stage of grafting follows first order kinetics at irradiation time \( t < 41.5 \) min and the second stage follows 1.7 order kinetics at 41.5-170 min. Overall reaction rate constants of \( 1.9 \times 10^{-3} \) and \( 2.87 \times 10^{-4} \) s\(^{-1}\) have been calculated for the samples grafted below and above 41.5 min respectively. The moisture content is found to increase linearly with the increase in graft yield up to 28% while the water uptake is linearly dependent on the logarithm of graft yield. Extremely high colour strength values are obtained when grafted PET samples are dyed in alkaline aqueous solutions at pH 11.5. A linear dependence is observed between the colour strength per graft yield and the logarithm of the pH of Rhodamine B Red and Astrazonrot Violet dye solutions. The dyeability of the fabric towards both the dyes increases suddenly as the graft yield increases to 2.5% followed by a transition up to 7% with a tendency to level off at degree of grafting higher than 10%. Thermal stability of irradiated, grafted and dyed samples has also been investigated by thermal gravimetric analysis to observe different degrees of fabric degradation as a result of irradiation, grafting and dyeing.

Keywords: Dyeing, Methacrylic acid, Moisture content, Polyester, Radiation grafting, Thermal analysis, Water uptake

IPC Code: Int. Cl. D06M 14/08

1 Introduction

Graft copolymerization is a well-known method for the modification of physical, thermal and chemical properties of polymer materials.\(^{17}\) Radiation grafting is most promising in vinyl graft copolymerization because of its large penetration in polymer matrix, and rapid and uniform formation of active sites for initiating grafting throughout the matrix.

Polymers not containing active sites such as PET can be radiation grafted to improve its hydrophilic properties by grafting hydrophilic monomers in the polymer matrix. Kale \textit{et al.}\(^{8}\) studied radiation grafting of acrylic acid (AA) and acrylonitrile (AN) onto polyester fibres and found that the AA grafted samples rendered more hydrophilic than the AN grafted ones for equivalent amount of grafts. Surface conductivity studies revealed that the number of polar groups increases with the increase of AA graft. Okada \textit{et al.}\(^{9}\) studied the radiation-induced graft copoly-merization of AA and MAA (methacrylic acid) onto PET fibres and found that the moisture regain is as that of cotton when changing PET-g-MAA to sodium methacrylate.

Stumett \textit{et al.}, Liepins \textit{et al.}, and Zahran \textit{et al.}\(^{12}\) studied the radiation grafting of various phosphorus and bromine containing vinyl monomers onto polyester, cotton and their blends to impart flame-resistant and flame-proofing characteristics. The graft yield was enhanced by the mutual peroxide and pre-irradiation method. Addition of 10% styrene to \(2,3\)-dibromopropylacrylate (DBPA) was found to avoid rapid and complete homopolymerization while addition of 10% MAA gave good grafting yields.\(^{12}\) Similar investigations on grafting flame retardants onto PET/cotton blends by electron beam-induced grafting were reported by Choi \textit{et al.}, Kong \textit{et al.}, and Kaji \textit{et al.}.\(^{14}\) Nor\(^{16}\) reported that according to DSC measurements the melting temperature of grafted PET fibres decreases slightly as the percentage of grafting increases. The difficulty in obtaining reasonable graft yield during grafting vinyl monomers onto PET fabric is quite obvious. Several authors have used electron beams to induce grafting.\(^{10,12,15,17,18}\) Zahran \textit{et al.}\(^{12}\) used the natural peroxide and pre-irradiated method while Kong \textit{et al.}\(^{14}\) used high doses and pre-swelling agents. Nor\(^{16}\) reported that formic acid is most effective in grafting AA onto polyester fibre.

The dyeability of PET fibre towards dyestuffs other than disperse dyes is almost impossible. Generally, it is difficult to dye PET fibre because of its high fibre crystallinity, marked hydrophobic properties and absence of chemically reactive groups. Attempts to

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improve the dyeability of PET fibre towards disperse dyes were made to overcome the low dyeing rate. This was achieved by building up dye molecules inside polyester (azoic dyeing), opening up the fibre structure to bring down $T_g$ (carrier dyeing), using temperatures above 100°C (high-temperature dyeing), or heating the dye in the dry state together with the fabric near the softening temperature (thermo-fixation dyeing). Several investigations using high dose rate radiation grafting techniques with electron beam accelerators\textsuperscript{10,16,17,19} have been carried out to graft and dye PET fibre with disperse dyes. Kale et al.\textsuperscript{8} showed that considerable improvement in the dyeability of PET fibre is possible through grafting with acrylic acid and acrylonitrile. About 50-100% improvement with disperse dyes was observed in case of polyester fibres containing 22.4% and 9% graft of AA and AN respectively.

It has been observed that the grafting of PET fibres requires special and developed techniques to reach reasonable graft yields to improve their properties. The present work was, therefore, undertaken to achieve considerable graft yields via gamma radiation grafting of methacrylic acid (MAA) onto PET in order to modify its hydrophobic, dyeing and thermal properties. The effect of solvents, swelling agents, MAA concentration and radiation dose on the graft yield has been studied. Dyeing of grafted samples with Rhodamine-B Red (RR) and Astrazonrot Violet (AV) basic dyes has been carried out and the effect of pH of the dye bath and graft yield on the colour strength studied.

2 Materials and Methods

2.1 Materials

Thermally stabilized (heat treated at 220°C for 1.5 min) low density polyester (PET) fabric, obtained from Hankook Synthetic Inc., Korea, was mill-scoured in a solution containing 0.001 g/L data scour WS-100 and 0.5 g/L sodium carbonate at boil for 1 h. The fabric was thoroughly washed with hot water, dried at ambient temperature and then used for grafting.

Methacrylic acid monomer, chloroform, methanol, acetic acid and Sandozin NIT liquid were used. Commercial Astrazonrot Violet (C.I. 48020) and Rhodamine Red (C.I. 45170) cationic/basic dyes, produced by Sandoz, were used.

2.2 Methods

2.2.1 Radiation Grafting

Grafting was carried out by the direct irradiation method in a \textsuperscript{60}Co gamma source of 1.98 Gy/s dose rate for different doses and MAA concentrations to achieve a wide range of graft yield. Dry weighed PET samples were impregnated with chloroform (swelling agent) for overnight before the introduction into wide mouth tubes provided with ground joint stoppers containing methanol solvent, monomer and 3 wt % (ows) of the grafting solution chloroform. About 0.7 g sample at a fabric-to-liquor ratio of 1:40 was then deaerated with bubbling nitrogen for 5 min.

2.2.2 Swelling Measurements

2.2.2.1 Water Uptake

Grafted and ungrafted fabrics of known weights were immersed in distilled water at ambient temperature till equilibrium reached. The samples were then removed and the excess water deposited on the surface was quickly removed with blotting paper and weighed. The samples were then dried to constant weight and the per cent water uptake was calculated from the difference in weights of wet and dry samples divided by the weight of dry sample.

2.2.2.2 Moisture Content

Grafted and ungrafted samples were left for conditioning at ambient temperature for 48 h before being weighed. The fabrics were then heated in a vacuum oven at 50°C till constant weight. The moisture content (%) was calculated from the difference in weights of moist and dry samples divided by the weight of moist sample.

2.2.3 Dyeing Procedure and Colour Strength Measurement

1% stock dye solution was prepared by making the paste of dye in acetic acid before the addition of required distilled water. Aqueous dye solutions containing 2% (owf) of dye were prepared from the dyestuffs at a fabric-to-liquor ratio of 1:50. The concentration of the dyeing solution was adjusted at $9.5\times10^{-4}$ mol/L. The pH of the dye bath was adjusted and the dyeing process was carried out in the presence of 1% (ows) sodium sulphate and few drops of 0.1 g/L Sandozin NIT liquid as a wetting agent. The temperature of the dye bath was then raised to 85°C and kept constant for 45 min. After dyeing, the samples were rinsed in hot water containing non-ionic detergent, followed by tap water rinse and then dried.

A computerized micro colorimeter unit\textsuperscript{2} was used for colour measurements. The $L^*, a^*$ and $b^*$ system used is based on the CIE-colour Triangle (Commission International de l'Eclairage Units X, Y and Z). In this system, the $L^*$ value represents the
dark-white axis, $a^*$ represents the green-red axis, and $b^*$ represents the blue-yellow axis. The $L^*$, $a^*$ and $b^*$ values of grafted fabrics before dye sorption were measured and taken as a reference. The colour difference ($\Delta E^*$) intensity of the grafted samples after dyeing was determined by the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \ldots \quad (1)$$

### 2.2.4 Thermal Gravimetric Analysis

The TGA study was carried out on a Shimadzu 30 (TGA-30) at a heating rate of 5°C/min in nitrogen atmosphere over a temperature ranging from room temperature to 500°C. The primary TGA thermograms were used to determine the effect of different treatments on the thermal stability of PET samples. The degree of conversion and weight remain of the sample are calculated as per the following relationship:

Degree of conversion (%) = $$\frac{(W_o - W_f)}{W_o} \times 100$$ \quad \ldots \quad (2)

Weight remain (%) = $$\frac{W_f}{W_o} \times 100$$ \quad \ldots \quad (3)

where $W_o$ and $W_f$ are the weights of the original and heated sample respectively.

### 3 Results and Discussion

#### 3.1 Graft yield

The difficulty in obtaining reasonable graft yield onto PET fibre was tackled by studying the factors affecting the grafting process. Preliminary experiments were carried out using water, methanol, ethanol, acetone and dimethyl formamide as solvents and swelling agents. Table 1 shows the effect of different types of solvents on the degree of grafting of PET fabric immersed in 10% MAA solutions at 1:40 fabric-to-liquor ratio and irradiated at 296 K temperature with 10 kGy dose using 1.98 Gy/s gamma dose rate. All the samples were kept immersed overnight in their solutions before being irradiated. The results indicate that the degree of grafting varies from 0.5% for dimethyl formamide to 1.73% for methanol. Observation of the grafting solutions after irradiation shows different degrees of homopolymerization varying from a heavy one in water to a very low one in methanol, ethanol and dimethyl formamide. The homopolymerization is followed by measuring the coefficient of viscosity from the shear stress-shear rate relationship. The low graft yield directed the attention to look for different swelling agents used such as chloroform and formic acid\(^{16}\). Tables 2 and 3 show the results for overnight immersion of the fabric in chloroform and formic acid before the preparation of grafting solutions. It is observed that pre-swelling of the fabric in chloroform and formic acid gives 2.18% and 0.9% graft yield respectively for 10% MAA irradiated to 10 kGy dose. Pre-swelled sample in chloroform irradiated to 10 kGy dose in solution containing 40% MAA gives 19.8% graft yield without homopolymer formation. Further attempts to improve the graft yield were made by adding chloroform in the grafting solution. Fig. 1 shows the effect of different chloroform concentrations on the degree of grafting of PET fabric. It is shown that the graft yield of samples irradiated to 10 kGy dose in 30% MAA concentration increases from 7.5% to 8.4% upon the addition of 3%
(ows) chloroform. Further increase in chloroform results in a decrease in graft yield to 6%. Consequently, all PET samples were immersed in chloroform for overnight before the addition of methanol solvent containing 3% (ows) chloroform at a fabric-to-liquor ratio of 1:40.

The immersion of PET fabric in chloroform as a swelling agent and its addition to the solvent-monomer solution results in opening the structure of PET and allows for the diffusion of monomer solution into the fibre matrix. This results in the enhancement of graft yield and consequently the occurrence of homogeneous grafting on the entire structure of fabric.

3.2 Reaction Order and Rate Constant

The dependence of degree of grafting of PET fabric on irradiation time (t) for MAA concentrations of 10-40 wt% is shown in Fig. 2. The figure shows two main grafting stages: (i) initial stage at irradiation time less < 41.5 min, and (ii) second stage at 41.5-170 min. The initial grafting rates are lower than those of the second stage and are monomer concentration dependent. Fig. 3 shows logarithmic plots of grafting rate ($R_g$) versus monomer concentration for both the grafting stages. The relationship is linear and indicates that the grafting rates follow a first and 1.7 order kinetics for the initial and second stages respectively. The overall reaction rate constant (k) for the initial and second stages are obtained from the plots of grafting rate versus MAA concentration to the powers 1 (Fig. 4) and 1.7 (Fig. 5) respectively. The slope of the straight line relationship gives the value of k. The values of k for the initial and second stages are $1.9 \times 10^{-5}$ and $2.87 \times 10^{-4}$ s$^{-1}$ respectively. This indicates that the second stage of grafting is 15 times faster than the initial stage. The equations governing the grafting rates to MAA concentration are as follows:

$$R_g \text{ (s}^{-1}) = 1.9 \times 10^{-5} [\text{MAA}] \text{ at } t < 41.5 \text{ min} \quad \cdots (4)$$

$$R_g \text{ (s}^{-1}) = 2.87 \times 10^{-4} [\text{MAA}]^{1.7} \text{ at } t 41.5-170 \text{ min} \quad \cdots (5)$$

At irradiation time $t > 170$ min, the degree of grafting shows tendency to level off.
3. Hydrophilic Properties

3.3 Moisture Content and Water Uptake

The moisture content measurement for MAA-g-PET fabric is shown in Fig. 6. The moisture content increases linearly from 0.05% for ungrafted fabric to 1.9% as the degree of grafting increases to 30%. The increase in moisture content with the increase in graft yield (GY) is due to the introduction of hydrophilic COOH functional group of MAA monomer in the structure of grafted PET fabric as well as by the accessible regions created by the bulky graft chains in the fibre structure. The higher the degree of grafting the higher is the number of carboxylic group. The slope of Fig. 6 (0.063% increase in moisture content per GY) is a measure of degree of hydrophilicity of the grafted fabric which is dependent on the type of grafted monomer.

The water uptake is found to increase with the increase in degree of grafting of MAA onto PET fabric. It increases from 6.5% for ungrafted fabric to 39% for 5% grafted samples. Further increase in graft yield to 10% increases the water uptake to 50%. The water uptake value reaches 67% at 30% graft yield. These results do not give logical understanding of the dependence of water uptake on graft yield. A mathematical relationship between the water uptake and degree of grafting is made by plotting the water uptake values vs the logarithm of graft yield. Fig. 7 shows a linear dependence and the equation governing the two parameters is presented as follows:

\[
\text{Water uptake (\%)} = 18.43 \ln (\text{GY \%}) + 6.43 \quad \ldots (6)
\]

The slope of the relationship (18.43) is a measure of increase in the water uptake by the increase in natural logarithm of degree of grafting and indicates the magnitude of hydrophilicity due to the grafting of MAA onto PET fabric. The value of intercept (6.43%) corresponds to the water uptake of ungrafted PET fabric. Eq (6) applies only to MAA-g-PET fabric and helps in the prediction of water uptake at any degree of grafting. This equation also indicates that the effect of carboxylic groups introduced in PET fabric is logarithmic and its value, as measured by the slope of the relationship, is dependent on the type of grafting monomer.
It is obvious from the results of dependence of moisture content and water uptake on the degree of grafting that the hydrophilic properties improve by the increase in degree of grafting of MAA onto PET fabric. The improvement in hydrophilic properties because of the introduction of carboxylic groups into the structure of nylon-6 and cotton fabrics has already been studied\textsuperscript{5,7} and is found to be in good agreement with the findings of Taher et al.\textsuperscript{20,21} and Hegazy et al.\textsuperscript{22,24}.

3.4 Dyeing Properties

3.4.1 Effect of pH on Dyeability of Fabric

The effect of pH of Astrazonrot Violet (AV) and Rhodamine Red (RR) dye solutions on the colour strength ($\Delta E$) of grafted PET fabric is shown in Fig. 8. The figure shows a correlation between the colour strength (CS) per graft yield (GY) of the dyed fabric and the logarithm of pH of the dye solution. Linear relationship is obtained for both the dyes. The empirical equation relating the CS/GY to the pH for both dyes is as follows:

\[(CS/GY)_{\text{RR dye}} = 20.50 \log \text{pH} - 10.8 \]  \hspace{1cm} (7)
\[(CS/GY)_{\text{AV dye}} = 12.26 \log \text{pH} - 1.2 \]  \hspace{1cm} (8)

The straight line intercepts the pH axis at 3.2 and 1.1 for RR and AV dyes respectively where the CS/GY is zero. It is clear from the equations that the slope of RR dye (20.50) is higher than that of AV dye (12.26). This indicates the faster response of RR dye to changes in pH. The difference in CS/GY between both dyes decreases with the increase in pH reaching almost the same value at pH 11.5. Consequently, all dyeing experiments were carried out at pH as close as possible to 11.5 for both dyes.

3.4.2 Effect of Degree of Grafting on Dyeability of Fabric

The effect of degree of grafting on the colour strength of PET fabrics dyed in AV and RR dye solutions of pH 11.5 is shown in Fig. 9. The results show fast linear increase in colour strength up to 91 and 67 for AV and RR dyes respectively as the GY increases to 2.5%. The initial rate of increase of colour strength with the increase in graft yield amounts to 36 and 27 CS/GY for AV and RR dyes respectively, indicating the higher affinity of AV dye
to MAA-g-PET fabric. Further increase in GY shows a decrease in rate of change of colour strength with a tendency to level off at graft yields higher than 10%. These results indicate that the dyeing of grafted PET fabrics in AV dye solutions gives CS values higher than those in RR solutions having the same degree of grafting. This supports the results presented in Fig. 8 and emphasizes the higher affinity of grafted PET fabric towards AV dye if compared with that of RR dye.

3.5 Thermal Properties

3.5.1 Effect of Radiation Dose on TGA Thermograms

The TGA thermograms of the effect of radiation dose on PET fabric show that the general feature of weight % remain as a function of temperature at a constant heating rate of 5°C/min is the same except that the curves shift to the left (lower temperature) as the radiation dose increases. The results indicate no significant effect of dose on the degradation of PET fabric up to about 325 °C. Further increase in temperature results in a rapid increase in fabric degradation which terminates at around 450°C. The temperature corresponding to 50% conversion (T₅₀%) is considered a measure of thermal stability of the fabric. The value of T₅₀% decreases from 425°C to 404.3°C as the irradiation dose increases to 30 kGy. The high T₅₀% value of unirradiated PET fabric indicates a high thermal stability even when heated above its melting point (258°C).

3.5.2 Effect of Grafting on TGA Thermograms

The effect of degree of grafting on the TGA thermograms is shown in Fig. 10. It is apparent that the T₅₀% decreases slightly from 425°C for unirradiated samples to 418.6°C for PET-g-PMMA. Increasing the degree of grafting from 12.7% to 26% does not show any change in the value of T₅₀%. This indicates that the grafting has no effect on the high temperature (>375°C) thermal stability of the fabric. The observed shift in the thermograms to lower temperatures in the high temperature range is mainly due to the irradiation dose at which grafting was carried out. Irradiating ungrafted PET at doses of 10 and 20 kGy shifted the T₅₀% of unirradiated samples to 419.6 and 411.7°C respectively. Since grafting was
carried out between these doses, one would expect radiation degradation in the samples. Comparison of \( T_{50\%} \) of grafted fabric (418.5°C) with that of irradiated fabric indicates that the degradation is due to irradiation rather than grafting.

Grafting, however, increases the degree of conversion (per cent weight loss) of the fabric below 375°C. The degree of conversion increases with the increase in grafting (Fig. 10). The difference in the weight % remain of the thermograms for 12.7% and 26% grafted samples disappears at around 375°C. This indicates the termination of the effect of grafting on thermal properties of PET through the complete dehydration of absorbed water occluded in the grafted copolymer (Fig. 6) as well as the entire degradation of MAA copolymer. Further increase in temperature results in the rapid degradation or decomposition of the whole PET polymer chain in a way similar to that for irradiated samples.

3.5.3 Effect of Dyeing on TGA Thermograms

The effect of dyeing on the thermal stability of AV and RR dyes is shown in Fig. 11. Fig. 11a shows thermograms for PET fabric grafted to 7.5% and 26% followed by dyeing with AV dye. The thermograms show that the dyeing of 7.5% grafted samples increases the degree of conversion of ungrafted samples by 11.7%. As the degree of grafting increases to 26% a significantly high increase in conversion (36%) occurs at 400°C. The difference in conversion for dyed samples having different graft yields decreases with the further increase in temperature tending to zero close to \( T_{50\%} \) value. The \( T_{50\%} \) of dyed samples is the same as that of grafted and irradiated samples.

Figure 11b shows thermograms of PET fabric grafted to 7.16% and 29.3% and dyed with RR dye. It is clear from the curves that the features of the thermograms for 7.16% grafted and dyed samples are the same as that of unirradiated sample at all temperature range with almost the same value of \( T_{50\%} \). The degree of conversion of 7.16% grafted samples amounts to 3.9% at 300°C. The slight difference between both thermograms is due to the increase in moisture content because of grafting. Dyeing of 29.3% grafted PET samples results in a noticeable decrease in conversion when compared with those of equivalent degree of grafting or AV dyeing. The difference between RR dyed samples having different graft yields vanishes above \( T_{50\%} \). About 30% of the total weight loss (7.16%) is due to the removal of moisture content (Fig. 6). The thermograms at higher temperature follow the decomposition curves as those of unirradiated and 10 kGy irradiated samples.

The above findings for AV and RR dyes show significant deterioration in the thermal properties of PET fabric for the dyeing with AV dye at < 400°C. RR dyeing of grafted samples, however, improves the thermal stability of the fabric over that of grafted one at low and high degrees of grafting and the degree of improvement depends on the amount of dye uptake. These results stress the importance of the study of thermal stability of dyestuffs themselves specially those used in tropical countries. Dyes with high thermal stability or high degree of crystallinity are expected to deteriorate the thermal properties of grafted PET fabric.

4 Conclusions

4.1 Pre-swelling of PET fabrics by overnight immersion in chloroform enhances the graft yield.

4.2 The initial grafting process follows first order kinetics at irradiation time (t) < 41.5 min followed by 1.7 order kinetics at 41.5-170 min.

4.3 The moisture content of PET fabric increases linearly with the increase in degree of grafting. The water uptake increases linearly with the increase in logarithm of graft yield.

4.4 The CS/GY of PET fabric dyed with RR and AV increases linearly with the increase in logarithm of pH of the dye solution, reaching the highest value at pH 11.5 and almost zero value at pH 3.2 and 1.1 for RR and AV dyes respectively.

4.5 The dyeability of grafted PET fabric towards RR and AV dyes initially increases with the increase in graft yield at 27 CS/GY and 36 CS/GY for RR and AV dyes respectively followed by a transition between 2.5% and 7.5% grafting with a tendency to level off above 10% graft yield. The deep shades of PET fabric dyed with RR and AV dyes are obtained at graft yields higher than 5%.

4.6 Irradiation decreases the thermal stability of ungrafted fabric at temperatures higher than 300°C.

4.7 Grafting deteriorates the thermal properties of PET samples and the degree of conversion depends on the graft yield. This effect is localized between 200°C and 375°C.

4.8 Dyeing of grafted samples affects the thermal properties of PET fabric, depending on the type of dye and temperature range. AV dye deteriorates the properties significantly while RR dye improves the thermal stability of the fabric. The degree of improvement increases with the increase in the amount of RR dye uptake.
Acknowledgement

The author is thankful to Prof. I A El-Shanshoury, NCRSRC, Atomic Energy Authority, Cairo, Egypt, for valuable assistance during the course of this work.

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