Effect of Graft Copolymerization of 2-Hydroxyethyl Methacrylate on the Properties of Polyester Fibers and Fabric

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Synopsis

Graft copolymerization of hydroxyethyl methacrylate (HEMA) onto poly(ethylene terephthalate) (PET) fibers using benzoyl peroxide (BP) as initiator was carried out in water and in water/organic solvent as a reaction medium. The effect of initiator concentration, reaction time, temperature, and reaction medium as well as addition of $FeSO_4$ to the polymerization medium was studied. Percent grafting was enhanced significantly by increasing BP concentration up to 0.016 mol/L and then decreased upon further increase in initiator concentration. Increasing the monomer (HEMA) concentration up to 0.48 mol/L improves significantly the graft yield. Raising the polymerization temperature up to 85°C causes a significant increase in grafting yield; further increase in temperature leads to decrease in graft yield. Incorporation of Fe^{+2} ions in the polymerization system decrease the graft yield. The same situation is encountered when water/solvent mixture is used as reaction medium. Solvent employed were methanol, toluene, and benzene.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are hydrophobic in nature and do not contain chemically reactive groups. For these reasons, this material is not easily penetrated by dyes of large molecular dimensions and cannot combine with dye either anions or cations. Certain desirable properties such as improvement in dyeability, increase in moisture regain, and improved mechanical properties as well as thermal properties can be imparted to PET fibers by graft copolymerization of these fibers with vinyl acetate[1], 2-methyl-5-vinyl pyridine,[2] acrylic acid,[3] and methyl methacrylate.[4-6]

Vinyl graft copolymerization onto PET could be initiated by high energy radiation using γ-rays from Co60[7,8] or by chemical means using different initiators such as benzoyl peroxide,[2,3] hydrogen peroxide,[4] pentavalent vanadium ion,[9] hexavalent chromium ion,[10] thallium(III),[5] tetravalent cerium,[6] and KMnO4/oxalic acid redox system.[4]

In the present paper graft copolymerization of hydroxyethyl methacrylate onto PET fibers and fabric using benzoyl peroxide (BP) as an initiator was carried out with a view of studying the conditions which affect the extent and the rate of polymerization. In addition, the effect of incorporation of metallic ions and solvents in the polymerization system on the graft yield and homopolymer formation was investigated.

Also, the effect of grafting on mechanical properties and moisture regain was investigated.

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EXPERIMENTAL

Materials

(a) Poly(ethylene terephthalate) fibers (Trevera, Hoechst, West Germany) and fabric woven from 100% polyester filaments.

(b) Benzoyl peroxide was purified by dissolving it in chloroform followed by addition of methanol (twice volume).

(c) 2-hydroxyethyl methacrylate (Aldrich) was purified from the inhibitor by passing through a column of alumina base.

The swelling agents, 1,2-dichloroethane and 1,1′,2,2′-tetrachloroethane and other solvents used during this work were of pure grade chemicals. Ferrous Ammonium sulfate $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ was of analytical grade.

Techniques

Graft Polymerization Procedure

The polyester was first swollen at 90–95°C for 2–3 h in the solvent–nonsolvent system consisting of either 1,2-dichloroethane/water (20/80 v/v) or tetrachloro-ethane/water (20/80 v/v).

Dichloroethane was removed from the fiber completely by treatment with boiling water. Tetrachloroethane was removed by treatment first with boiling alcohol and then with boiling water. The swollen fibers were used for grafting.

Two-step grafting of the monomer onto PET was carried out as follows:

The first step was the pretreatment of 1 g polyester with the monomer and 0.016 mol/L bezoyl peroxide in 5 mL benzene for 12 h. Benzene acts as a medium for dispersing benzoyl peroxide.

The second step was the addition of 95 mL distilled water, and the grafting was carried out at the temperature of 85°C for 4 h with continuous stirring. After that the grafted polyesters were washed with boiling methyl alcohol until the homopolymer was practically removed, the samples were then dried at 100°C for 1 h, then over P_2O_5 in dissicator and weighed.

Total weight of the homopolymer recovered from the grafting solution as well as extracted from PET matrix was determined after removal of the solvent by distillation under vacuum. The remaining homopolymer was dried in an oven at 120°C for 4 h and then cooled in a desiccator.

Both grafted fibers and homopolymer were dried till constant weight. Percent of "graft" yield and homopolymer was calculated according to the following relations:

$$\% \text{ "graft" yield} = \frac{\text{wt grafted sample} - \text{wt original sample}}{\text{wt original sample}} \times 100$$

$$\% \text{ homopolymer} = \frac{\text{wt homopolymer}}{\text{monomer used}} \times 100$$

Determination of Tensile Strength

The tensile strength of the polyester and grafted polyester was evaluated by using Uster Ten 50 mat II type according to a standard method.[11]

Determination of Moisture Regain

The moisture regain of the polyester and grafted polyester was evaluated by using an FL.02 type according to a standard method.[11]

DSC Measurements

DSC measurements for polyester and grafted polyester fabric were carried out by using DSC technique (DSC 111 J. Y. France) at the Central Laboratory, Mansoura University.

RESULTS AND DISCUSSION

Effect of Temperature on the "Graft" Yield

Figure 1 shows the effect of polymerization temperature on the grafting yield on fibers. It is clear that the "graft" yield increases with increasing the temperature from 65 to 85°C; further increase in the temperature decreases the "graft" yield. The enhancement in grafting upon raising the polymeriza-
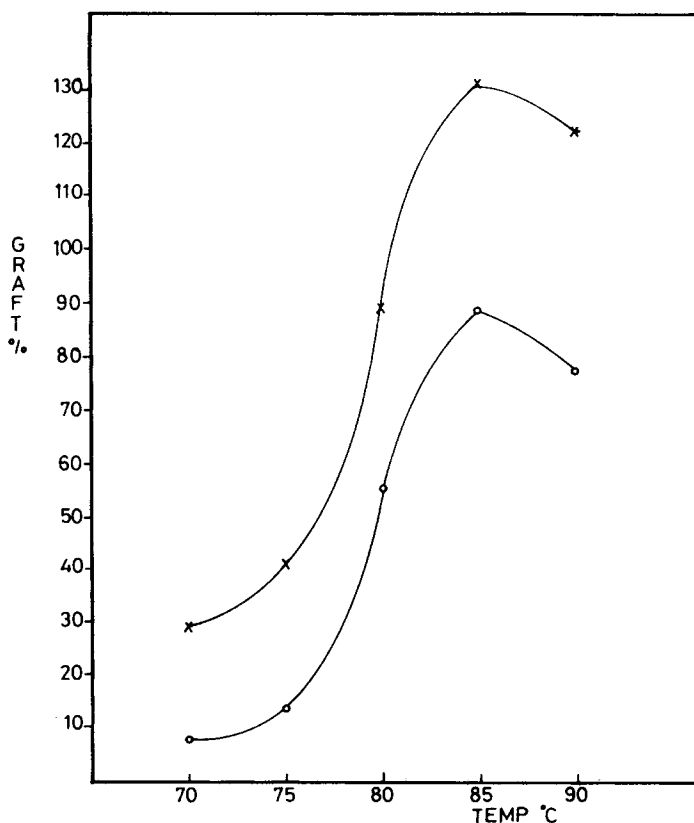

Fig. 1. Effect of temperature on graft yield of HEMA on polyester fibers: time = 4 h; [BP] = 0.016 mol/L; [HEMA] = 0.48 mol/L; PET : solvent = 1 g : 100 mL; (o) fibers; (×) fabric.

tion temperature from 65 to 85°C could be ascribed to:

(1) higher rate of BP decomposition;

(2) possible reaction between the growing homopolymer chain radical with PET.

The net effect of all these factors is certainly increased grafting, whereas lowering of grafting by raising the temperature above 85°C could be ascribed to a fast rate of termination. Comparison between grafting yield on fibers and on fabric at the same conditions are shown in Figure 1, which shows higher "graft" yield in the case of fabric.

Effect of Initiator Concentration

Figure 2 shows that, within the range studied of BP concentration from 0.008 to 0.020 mol/L, the "graft" yield increases significantly by increasing the BP concentration up to 0.016 mol/L and then falls down upon further increase in BP concentration. The enhancement in "graft" yield by increasing BP concentration up to certain limit (0.016 mol/L) suggests that BP decomposes to yield benzoyl radicals which may undergo further reaction to yield ultimately phenyl radicals. These free radical species, i.e., benzoyl and phenyl
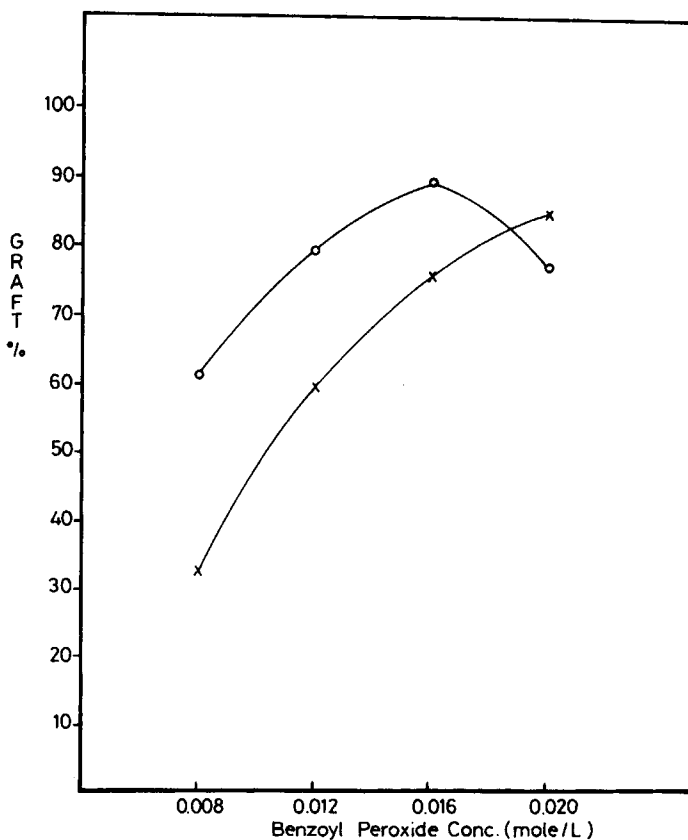
Fig. 2. Effect of initiator concentration on graft yield of HEMA on polyester fibers: time = 4 h; temp = 85°C; [HEMA] = 0.48 mol/L; (○) % graft yield; (×) % homopolymer; PET : solvent = 1 g : 100 mL.

radicals, are expected to increase by increasing the BP concentration. Direct abstraction of the hydrogen atom from the polyester backbone by these free radical as well as formation of similar PET macroradicals via chain transfer from growing homopolymer of HEMA chains seem to be in full swing at this particular concentration of BP (0.016 mol/L). Above this concentration, there will be abundance of free radicals which, besides contributing to the grafting, would terminate themselves by combination and/or cease the polyester macroradicals as well as growing grafted chain radicals, thereby leading to decreasing grafting. Unlike the "graft" yield, homopolymer increases significantly as the BP concentration increases within the range studied. Differences in the ability of BP in initiating and terminating the graft and homopolymerization would account for the results shown in Figure 2.

Effect of Monomer Concentration

Figure 3 shows the effect of monomer concentration on the grafting yield. It is shown that the grafting yield increases significantly as the monomer concentration increases. In addition, the increase of "graft" yield could be also associated with the gel effect brought about by the solubility of poly(hydroxyethyl methacrylate) in its own monomer. As a result, termination of the
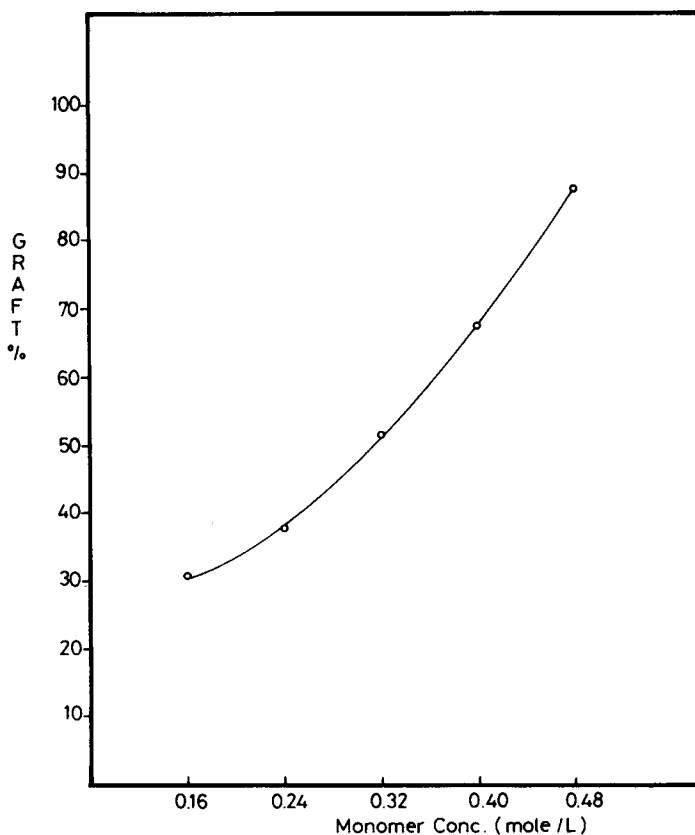

Fig. 3. Relation between graft yield and monomer concentration in the presence of polyester fibers: time = 4 h; temp = 85°C; [BP] = 0.016 mol/L; PET : solvent = 1 g : 100 mL.

growing grafted chain radical by coupling may be hindered. Besides, the gel effect perhaps causes swelling of PET fibers and facilitates diffusion of monomer to the growing grafted chains as well as formation of active sites on the PET backbone and thereby enhancing grafting.[4]

Effect of Polymerization Medium

The effect of different types of solvents such as methanol, toluene, or benzene and water/organic solvent mixtures on the "graft" yield in the presence of PET fabric was investigated. From Figure 4 it is shown that increasing the solvent ratio in the water/solvent mixture is accompanied by a significant decrease in the "graft" yield. The decrease in grafting yield including solvents in the reaction medium implies that these solvents are very likely to participate in termination of the grafted growing polymer chain. From the obtained results in Figure 4, it can be concluded that the affinity of the solvents used in decreasing the graft yield can be arranged in the following order:

$$\text{toluene} \geq \text{methanol} > \text{benzene}$$

[Such arrangement almost agrees with the order of decreasing chain transfer constants of the corresponding solvents in the polymerization of, e.g., methyl methacrylate at 80°C.[12]
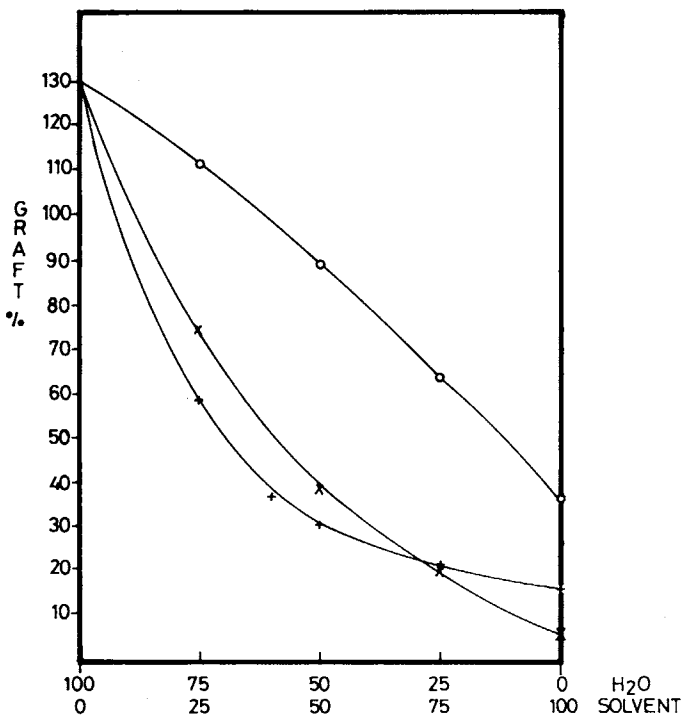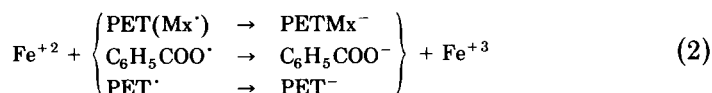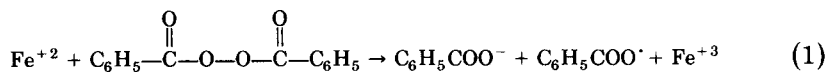

Fig. 4. Effect of type of solvent and different ratios of water/solvent mixture on graft yield of HEMA on PET fabric: time = 4 h; temp = 85°C; [HEMA] = 0.48 mol/L; [BP] = 0.016; PET : solvent = 1 g : 100 mL; (○) benzene; (×) toluene; (+) methanol.

Effect of Metallic Ions (Redox Systems)

The results described in Figure 5 shows the effect of ferrous ammonium sulfate concentration on grafting and homopolymer yield in the presence of PET fibers. It is shown that with increasing Fe^{+2} ion concentration from 0.2 to 1 mmol/L there is a decrease in grafting yield. This suggests that excess Fe^{+2} ions participate in the generation of free radical species [eq. (1)], and the Fe^{+2} ion also seems to contribute to the termination of free radical species [eq. (2)]:

$$Fe^{+2} + C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \rightarrow C_6H_5COO^- + C_6H_5COO^{\cdot} + Fe^{+3} \tag{1}$$

$$Fe^{+2} + \begin{Bmatrix} PET(Mx^{\cdot}) & \rightarrow & PETMx^- \\ C_6H_5COO^{\cdot} & \rightarrow & C_6H_5COO^- \\ PET^{\cdot} & \rightarrow & PET^- \end{Bmatrix} + Fe^{+3} \tag{2}$$

This is true for PET macroradicals as well as growing graft radicals.[13] The ultimate effect of termination is decreased grafting. Under the mentioned
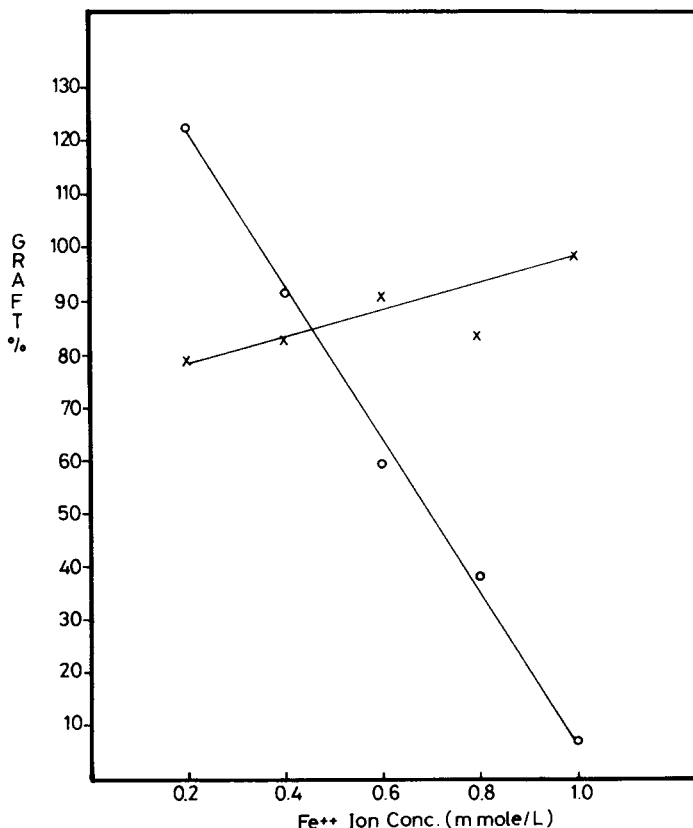

Fig. 5. Ferrous ammonium sulphate concentration vs. % polymer yield on polyester fiber: time = 4 h; temp = 85°C; [BP] = 0.016 mol/L; [HEMA] = 0.48 mol/L; PET : solvent = 1 g : 100 mL. Pretreatment with 0.2, 0.4, 0.6, 0.8, 1 mmol/L ferrous ammonium sulfate: (○) % graft yield; (×) % homopolymer.

condition, monomer, Fe^{+2}, and BP are present together in the polymerization solution. Hence, free radicals are generated in the aqueous phase rather than in the close proximity of PET. Consequently, the chance of a homopolymer formation is greater. Thus, the homopolymerization reactions prevail over the grafting reactions.

Evaluation of the Properties of the Grafted Samples

Mechanical Properties

The effect of grafting yield on the tensile strength of polyester fibers was evaluated and is represented in Figure 6. It is shown that the tensile strength value increases with increasing grafting yield up to 17% grafting. Also, the elongation of the fibers was considerably increased after grafting. This suggests that the grafted polymer masks most of the weak points of the fibers. Beyond 17% grafting, there is decrease in tensile strength and elongation. This decrease in tensile strength can be attributed to the decrease in the crystalline form as indicated by DSC diagram in Figure 7. However, the slight decrease in elongation could be due to the formation of hard segments of grafted part onto PET macromolecules.
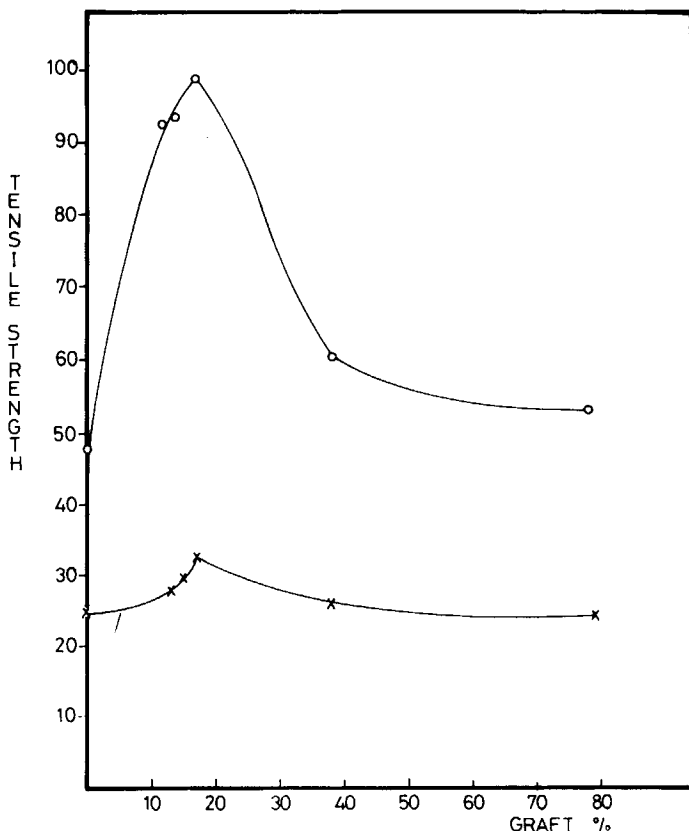

Fig. 6.   Effect of graft yield on mechanical properties of polyester fibers: (○) tensile strength (lb); (×) elongation %.
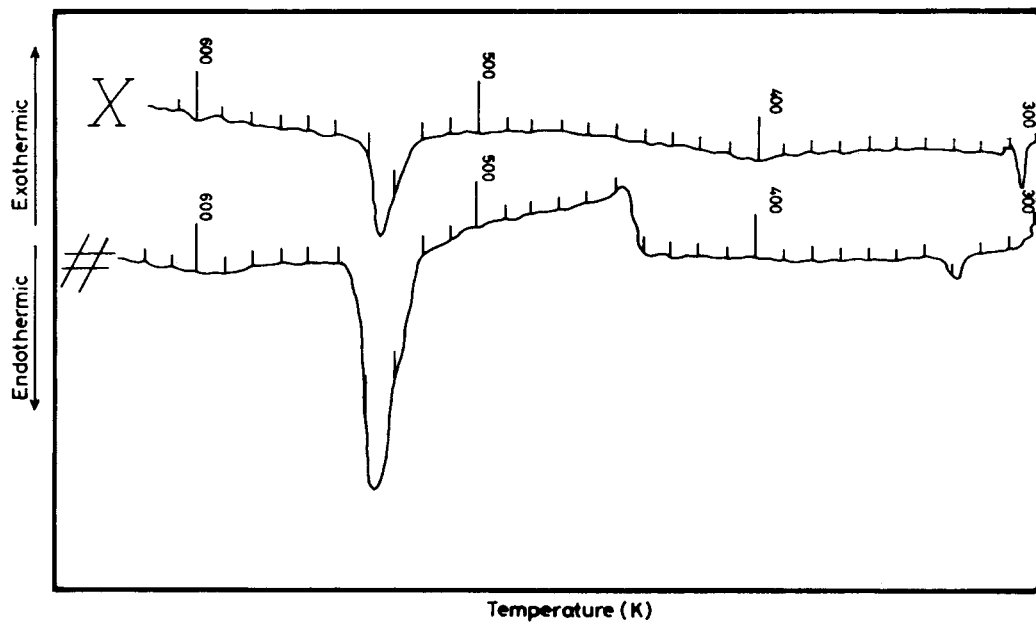
Fig. 7. (×) DSC diagram of PET fabric; (#) DSC diagram of HEMA-30% grafted PET fabric. Temperature range from 300 to 600 K.
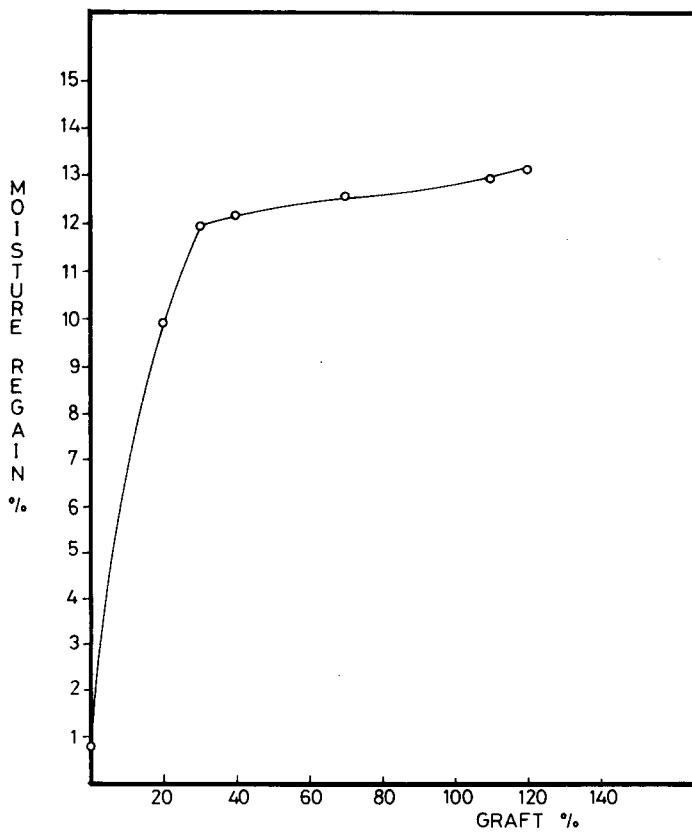
Fig. 8. Moisture regain % of HEMA-grafted PET fabric.

Moisture Regain

It is known that polyester fabric are hydrophobic in nature. Grafting with HEMA not only brings about the opening of the structure to a certain extent but also increases hydrophilicity of the polyester. This shift toward a hydrophilic nature is responsible for the increase in moisture regain from 0.6 to 12% as the "graft" percentage of HEMA is increased steadily up to 125%. The measured values of moisture regain are represented in Figure 8.

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