

## GRAFTING OF ACRYLAMIDE - METHACRYLIC ACID MIXTURE UPON POLY (ETHYLENE TEREPHTHALATE) FIBERS

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### SUMMARY

In this study the grafting of acrylamide-methacrylic acid monomer mixture upon poly (ethylene terephthalate) fibers using benzoyl peroxide as initiator was investigated. The increase of benzoyl peroxide concentration above 0.0968 g/50 ml decreased the graft yield. The variation of the graft yield with temperature was also investigated in the range of 65-92 °C. Maximum graft yield was obtained at a acrylamide-methacrylic acid mixture ratio of 50/50 (w/w). The monomers have a synergistic effect upon each other to take place in the graft copolymer.

### INTRODUCTION

Poly (ethylene terephthalate) (PET) fibers are one of the most important fibers used in Textile Industry today. But some of the undesirable properties of PET fibers such as low moisture regain and difficulty of dyeing limit its applications. One of the ways for improving these properties of PET fibers is, to graft a monomer upon them. By this way, it is possible to impart the properties of the polymer which forms the side branches to the PET fibers.

It is possible to graft more than one monomer upon PET fibers. By this way, the polymer branches consisting different functional groups enter the fiber structure. In recent years the number of studies concerning about grafting more than one monomer upon PET fibers at the same time increased. But most of these are patented literature. Therefore data about the conditions of graft copolymerization and the characterization of grafted fibers are not clear. There are a lot of examples of the grafting studies upon PET fibers using various monomer mixtures such as acrylamide-acrylonitrile (Yamauchi and Okamura 1973); methacrylic acid-acrylamide and methacrylamide-methacrylic acid

(Maeda 1973); acrylic acid-acrylonitrile and acrylic acid-methacrylonitrile (Sakurada et. al. 1975); acrylic acid-methylmethacrylate (Hataida et al. 1977); acrylic acid-styrene (Hebeish et. al. 1982).

The determination of the factors effecting the graft copolymerization conditions are as important as investigating the properties of grafted fiber.

The purpose of this study is to examine the grafting of acrylamide-methacrylic acid mixture upon PET fibers using benzoyl peroxide as an initiator.

## EXPERIMENTAL

**Materials:** Poly (ethylene terephthalate) (PET) fibers (multiflament, 110 Tex) used in the graft copolymerization were obtained from SASA Co. (Adana, Turkey). The fiber samples were cleaned by washing them for six hours in a Soxhlet device with acetone. Methacrylic acid (Ma) was kept for a day after being saturated with NaCl and then dried with  $\text{CaCl}_2$  and distilled in vacuum at  $41^\circ\text{C}$  (Perrin et. al. 1966). Other monomer acrylamide (Aam) was used as supplied without being subjected to any purification procedure. Benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ) was precipitated twice from chloroform solution in methanol and dried in vacuum dessicator for two days (Nozaki and Bartlett 1946).

**Polymerization Procedure:** After PET fibers ( $0.3 \pm 0.01$  g) had been put in a reaction tube (100 ml), monomer or monomers, 45 ml distilled water and benzoyl peroxide solution prepared in 5 ml crystalizable benzene were added to it. The mixture was placed into a water bath adjusted to the polymerization temperature immediately. Grafted fiber samples taken from the mixture after a specified time were washed with water at room temperature for 8 hours. Then they were washed with hot water for 4 hours by changing the washing water at least four times. They were finally extracted in Soxhlet device with water for six hours, before being dried and weighted. The increase in weight of the sample divided by its original dry weight and multiplied by 100 will be referred as graft yield (%).

The amount of acrylamide in the fiber samples grafted with Aam-Ma mixture was evaluated from the nitrogen determinations made by semi-micro Kjeldahl method. The amount of methacrylic acid which entered the structure was then calculated by subtracting the amount of acrylamide from the amount of graft yield.

## RESULTS AND DISCUSSION

The results obtained from the chemical grafting of Aam-Ma mixture upon PET fibers by the aid of benzoyl peroxide and the factors affecting the graft yield are as follows:

## POLYMERIZATION TEMPERATURE

Fig. 1 shows the effects of polymerization temperature and polymerization time upon the graft yield of grafting Aam-Ma mixture upon PET fibers. As seen from the figure the increase in the temperature, increases the grafting rate. There observed 3 and 2 hours of induction periods in the polymerizations carried out at 65 °C and 70 °C, respectively.

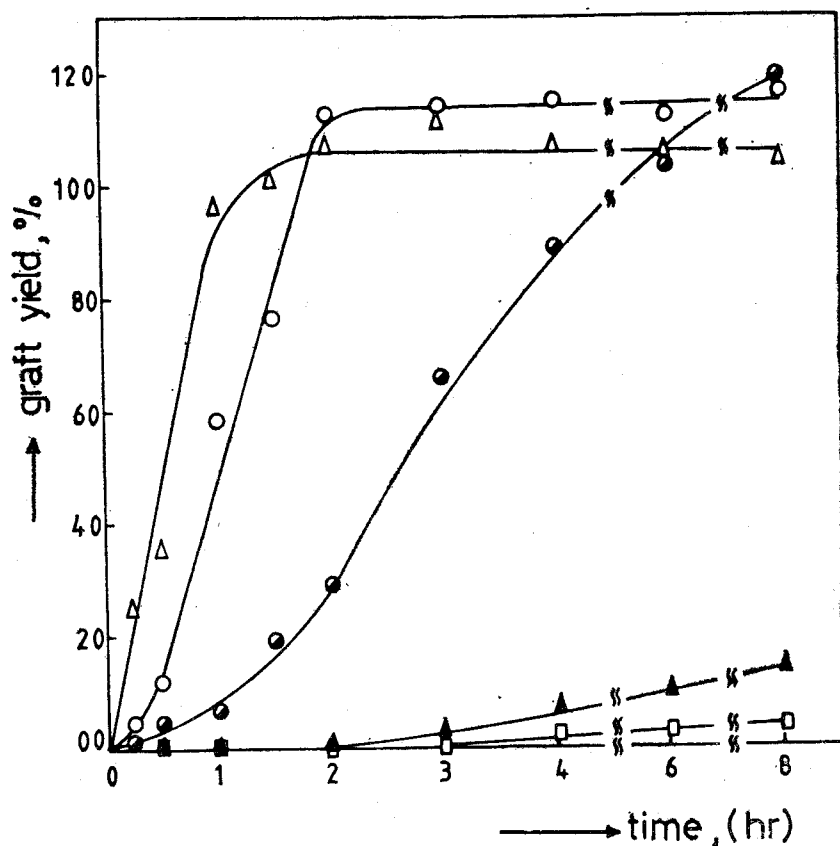


Fig. 1. Variation of graft yield with polymerization temperature:  $[Bz_2O_2] = 0.0484$  g/50 ml; monomer concentration, 2 g/50 ml; Aam/Ma, 60/40 (w/w); □, 65°C; ▲, 70°C; ●, 75°C; ○, 85°C; △, 92°C.

Schamberg (1970) stated that the maximum graft yield was reached at temperatures near the glass-transition temperature of the polymers grafted. The glass-transition temperature for PET is 80°C. The polymer chains become mobile near to glass-transition temperature and give radical reactions much more easily. As the temperature is increased the chain termination reactions start to predominate which causes more and more radicals to combine. Therefore the graft yield decreases due to these effects.

### INITIATOR CONCENTRATION

The variation of graft yield with the benzoyl peroxide concentration by keeping the ratio of Aam-Ma at 60/40 (w/w) was given in Fig. 2. It became clear that high graft yields would be obtained by keeping the initiator concentration in the range of 0.0484 g/50 ml to 0.0968 g/50 ml.

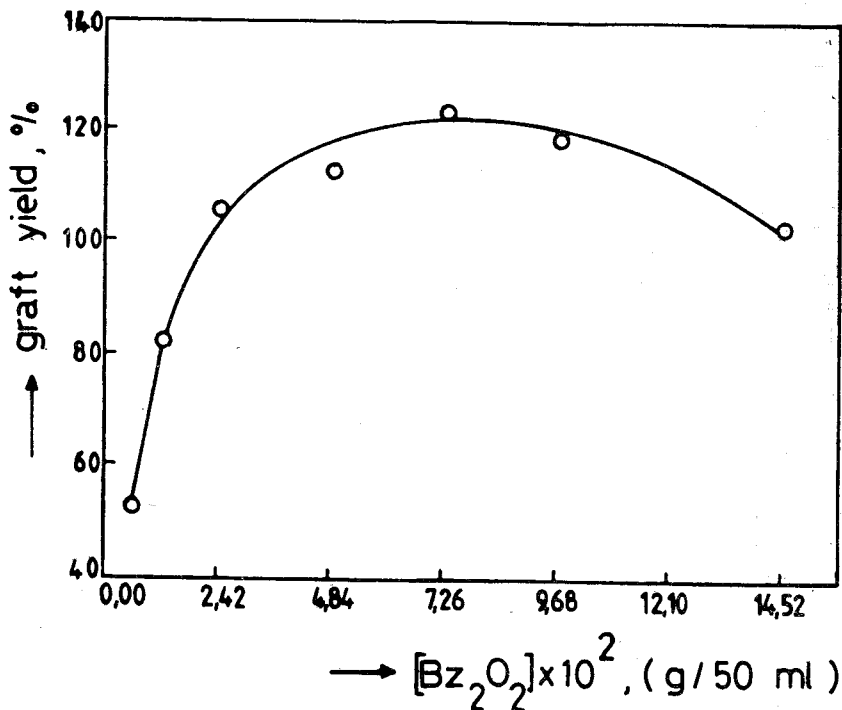


Fig. 2. Variation of graft yield with benzoyl peroxide concentration: temperature, 85°C; time, 2 hr; monomer concentration, 2 g/50 ml; Aam/Ma, 60/40 (w/w).

By increasing the concentration of benzoyl peroxide, one increases the free radical and polymeric radical concentration in the polymerization medium. This in turn causes an increase in the amount of grafting. Further increases in benzoyl peroxide concentration, increase the total radical concentration in the medium to a significant extent, which causes an increase in the rate of termination reactions. This situation slows down the rate of formation of active centers and decreases the graft yield.

### MONOMER CONCENTRATION

Fig. 3 shows the variation of graft yields of Aam, Ma and Aam-Ma mixture with the monomer concentration. As one sees from the figure

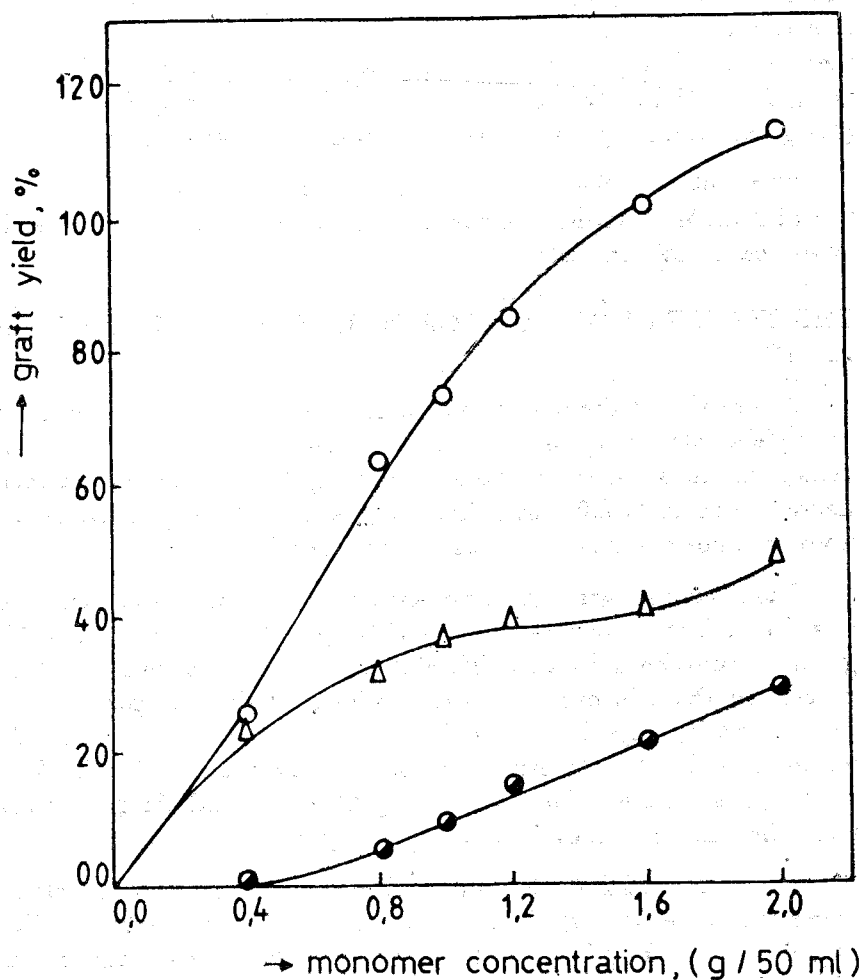


Fig. 3. Variation of graft yield with monomer concentration: temperature, 85°C; time, 2 hr;  $[Bz_2O_2] = 0.0484$  g/50 ml; Aam/Ma, 60/40 (w/w); O, Aam-Ma;  $\Delta$ , Ma;  $\bullet$ , Aam.

the grafting yield increases with the increasing monomer concentration. Therefore, if one increases the concentrations of the monomers, one has a greater number of monomer molecules available for the combination with the free radicals on the backbone of the polymer chain. It also favors the production of large number of growing homopolymer chains which increase the possibility of hydrogen-abstraction via chain transfer giving rise to active centers on the polymer backbone to be grafted. This leads to the increased extent of chain propagation, resulting in the greater degree of grafting.

As it is clearly seen from the figure that the use of Aam-Ma mixture increases the graft yield compared with use of Aam or Ma alone. For example, the graft yields obtained by using 2 g Aam or Ma monomers in 50 ml solution were 28.5 % and 48.5 % respectively while the graft yield resulted from the use of 2 g of 60/40 (w/w) mixture (1.2 g Aam and 0.8 g Ma) of these two monomers was 112.2 %.

The fact that the graft yield shows a marked increase with the use of Aam-Ma mixture compared with use of Aam or Ma alone, is explained below, in detail.

#### THE CHANGE OF GRAFT YIELD WITH THE Aam-Ma MIXTURE RATIO

The results of the experiments carried out to show the change of graft yield with change in monomer mixture ratio by keeping the monomer concentration constant is shown in Fig. 4. In figure the monomer mixture ratio of 80/20 shows that 1.6 g Aam and 0.4 g Ma monomer were used per every 50 ml of water-benzene solution.

The maximum graft yield for Aam together with Ma co-monomer was obtained at a monomer ratio of 50/50 (w/w) as 121.2 %. Aam-Ma grafting causes both Aam and Ma units enter the side chains. The Aam content in the side chains was determined by the nitrogen analysis carried out by Kjeldahl method. The amount of methacrylic acid which entered to the structure was determined by subtracting the Aam grafting content from the total grafting. The Aam and Ma graft yields using monomer mixtures for grafting in Fig. 5.

Figures 3 and 4 show that Aam and Ma monomers enter to the structure much more when grafted together than grafted individually. This experimental finding is in good compliance with the monomer reactivity ratios. The monomer reactivity ratios of Aam and Ma in the co-

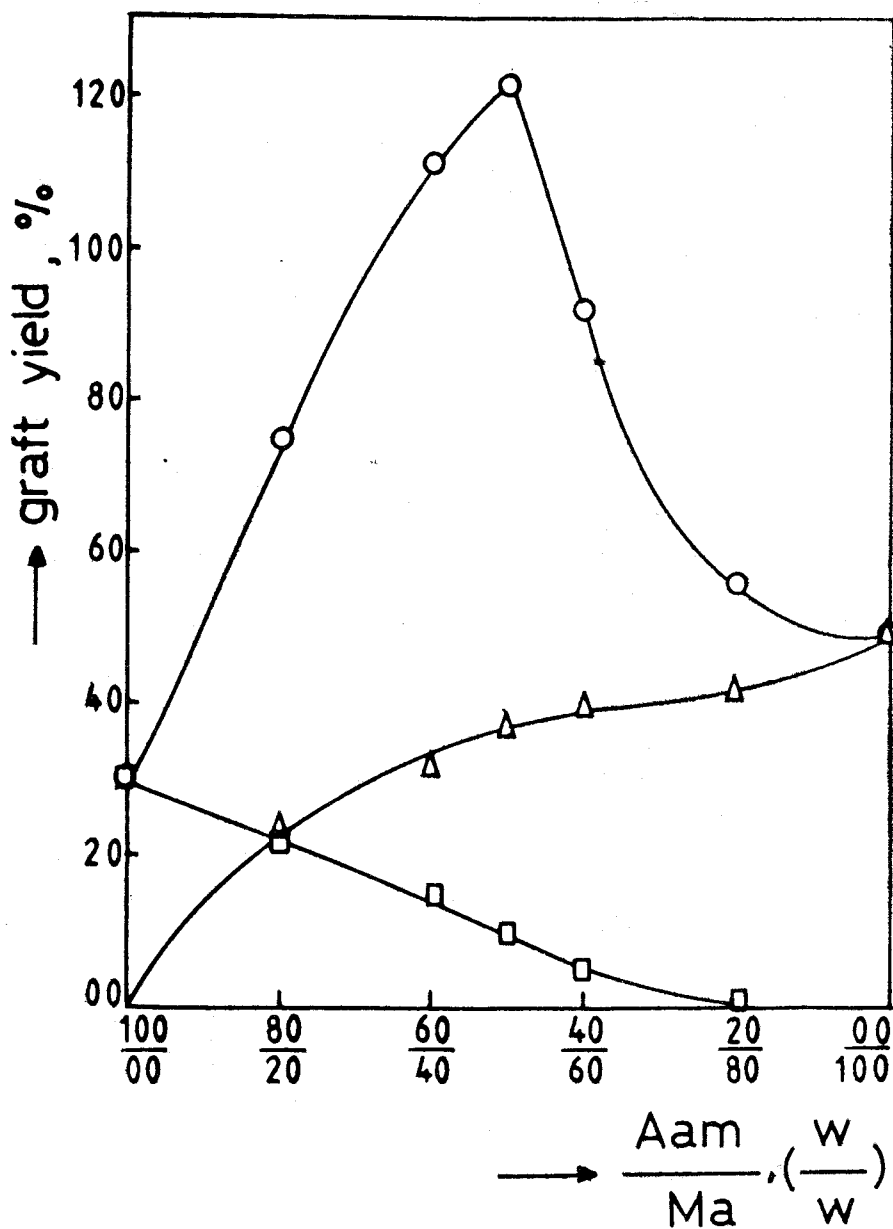


Fig. 4. Variation of graft yield with Aam-Ma ratio: temperature, 85°C; time, 2 hr; monomer concentration, 2 g/50 ml;  $[Bz_2O_2] = 0.0484$  g/50 ml; O, Aam-Ma, Δ, Ma; □, Aam.

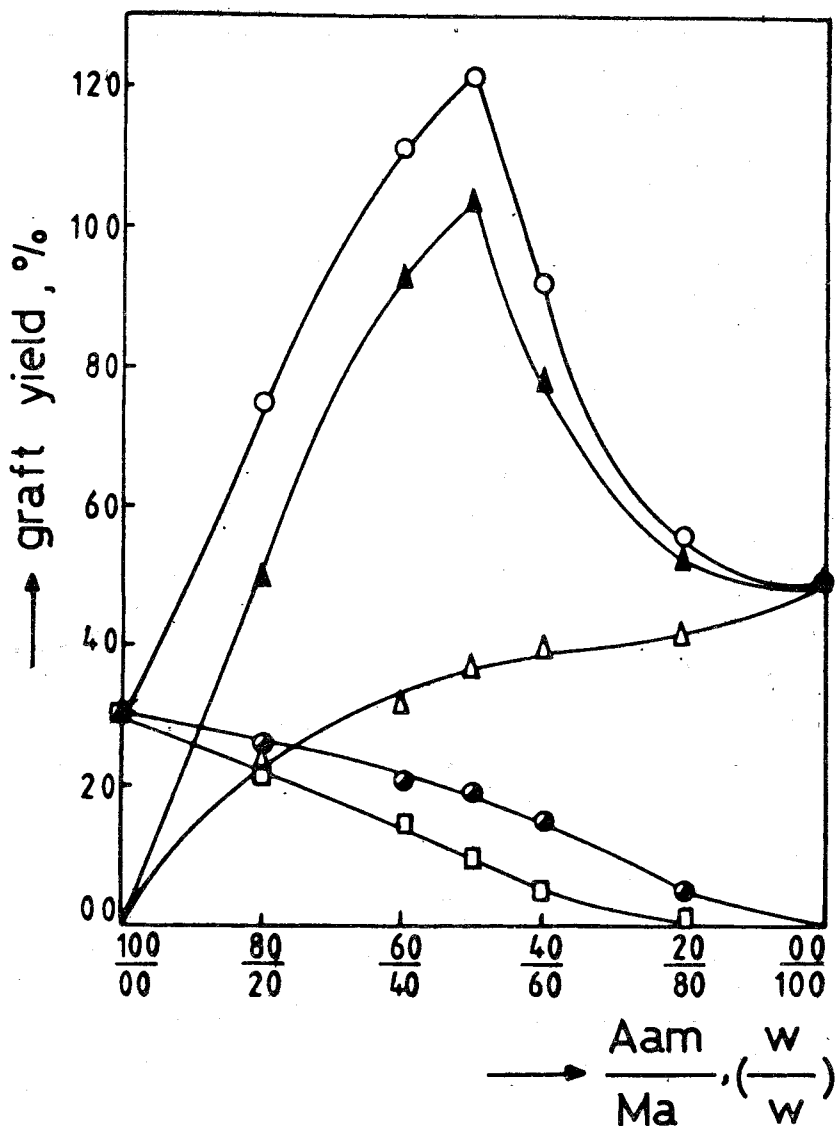


Fig. 5. Graft yields of Aam and Ma monomers obtained in mixtures and individually:  $[Bz_2O_2] = 0.0484$  g/50 ml; temperature,  $85^\circ C$ ; time, 2 hr; O, Aam-Ma; ▲, Ma (mixture); △, Ma (individual); ●, Aam (mixture); □, Aam (individual).

polymerization with each other are given in literature as 0.12 ( $r_1$ ) and 0.25 ( $r_2$ ), respectively (Brandrup and Immergut 1975).



These reactivity values signify that Aam and Ma monomer radicals prefer to react with each other rather than reacting with those of their own kind. Therefore, the possibility of enhanced reaction activity between Aam and Ma monomers and their graft copolymerization reaction with the PET fibers increase. Such a positive synergistic effect was observed in some grafting systems (Trivedi et. al. 1975, Hebeish et. al. 1982, Lokhande et. al. 1984).

Fig. 5 also shows that Ma units enter to the side chains much more than Aam. Odion et. al. (1961) observed that the polar monomer enters to the side chain structure more than non-polar monomer. Similar results were obtained in grafting of acrylamide-acrylic acid upon PET fibers (Lokhande et. al. 1984) and styrene-ethylacrylate upon wool (Garnett et. al. 1977). The results obtained in this study are also in agreement with those studies.

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