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SYNTHESIS OF METHYL-METHACRYLATE GRAFTED NATURAL RUBBER IN BULK PHASE

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ABSTRACT

Methyl-methacrylate grafted natural rubber was prepared at 40, 50, 60 and 70° C in the presence of benzoyl peroxide as thermal initiator and NN' dimethyl aniline as activator. From the gross copolymerisation product, the rubber-PMMA grafted inter polymer fraction was isolated from the free rubber and homopolymer. The efficiency of grafting under varied conditions has been discussed.

INTRODUCTION

THE graft copolymerisation of methyl-methacrylate (MMA) onto natural rubber can be carried out in solution, in latex or in bulk rubber swollen with the monomer. Considerable amount of literature is available on grafting of MMA with natural rubber in solution¹⁻⁵ and in emulsion using the latex rubber^{4,6-14}. However, very little is known about the reaction in bulk phase. Swift¹⁵ studied the graft copolymerisation of MMA with natural rubber in solid phase at 80° and 100° C. Ceresa¹⁶ has studied the grafting of acetone extracted and masticated natural rubber with MMA at 80° C and obtained grafted rubber. As dry rubber is easy to handle and transportation from place to place is not cumbersome when compared to latex, it is of interest to investigate the preparation of grafted rubber in a mass of dry rubber which has been allowed to imbibe the necessary quantity of monomer (MMA

in our case). The aim of this investigation was to ascribe the conditions obtained during such polymerisations and to evolve a process which works within the limitations imposed by these conditions. In this communication we present the results on the compositions of natural rubber MMA graft copolymerisation products under varied reaction conditions.

EXPERIMENTAL

A known amount of rubber (smoked sheet) was allowed to swell in a fixed volume of the monomer (MMA-distilled and free from inhibitors) containing a known amount of the initiator benzoyl peroxide (recrystallized) and activator (NN' dimethyl aniline boiling range 191-195° C) for about 24 hr in dark at room temperature (23 ± 2° C) under inert atmosphere. The polymerisation was carried out in a constant

temperature water bath ($\pm 0.1^\circ\text{C}$) at 40° , 50° , 60° and 70°C for 6 hr in all cases. To know the effect of reaction time on grafting efficiency, the reaction was carried out at 70°C and was arrested at different time intervals by precipitating the whole polymer with a large excess of methanol. The gross polymer was then filtered and separated from the unreacted rubber, polymethyl methacrylate (PMMA) and graft copolymer by selective extraction and precipitation technique². The separated fractions were then dried in vacuum oven at 45°C and weighed to a constant weight.

The amounts of natural rubber (2 g), benzoyl peroxide (0.01 g) and NN' dimethyl aniline (0.02 g) were kept constant during this investigation, while the amount of MMA was varied to give different monomer/rubber ratios.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the results of graft copolymerisation. It was found that some free rubber was always left behind at the end of the reactions. A

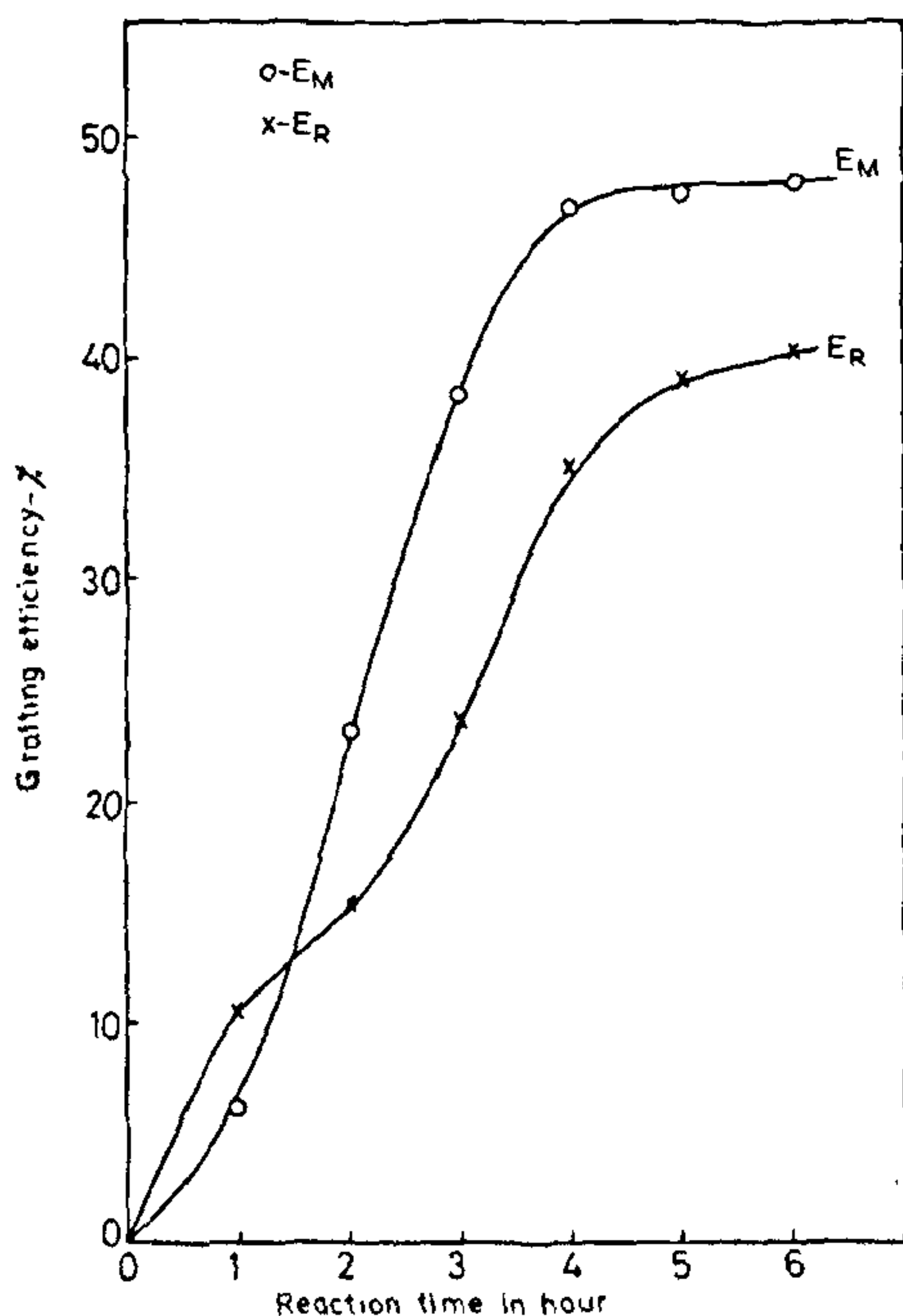


Figure 1. Relationship between reaction time and percentage grafting efficiencies E_M , E_R . Reaction temperature— 70°C , monomer—4 cc, rubber—2g.

small amount (0.12 ± 0.05 g) of the insoluble rubber was also obtained in all the experiments. This was separated out from the gross polymer at early stages of precipitation. This fraction was rejected.

The grafting efficiency based on rubber (E_R) is expressed as the percentage of total rubber appearing in the graft copolymer and that based on PMMA, E_M is expressed as the percentage of total PMMA appearing in the copolymer.

Figure 1 shows the effect of reaction time on E_M and E_R at 70°C and at monomer to rubber ratio of 1.88. With the increase in reaction time E_M and E_R increase and at later stages level off. E_M values after 4 hr of reaction show no appreciable change while E_R values show an increasing trend (35 to 40%) over the same period. This may be due to attachment of further rubber chain radicals to the grafted copolymer. In the early stages of reaction the trend was opposite and the rate of grafting of PMMA to natural rubber was very rapid.

Figures 2 and 3 show the effect of monomer concentration and reaction temperature on grafting efficiencies E_M and E_R , respectively. The E_M values decrease with increasing concentration of monomer at all temperatures, while E_R value increases. At particular monomer concentration, the increase in the

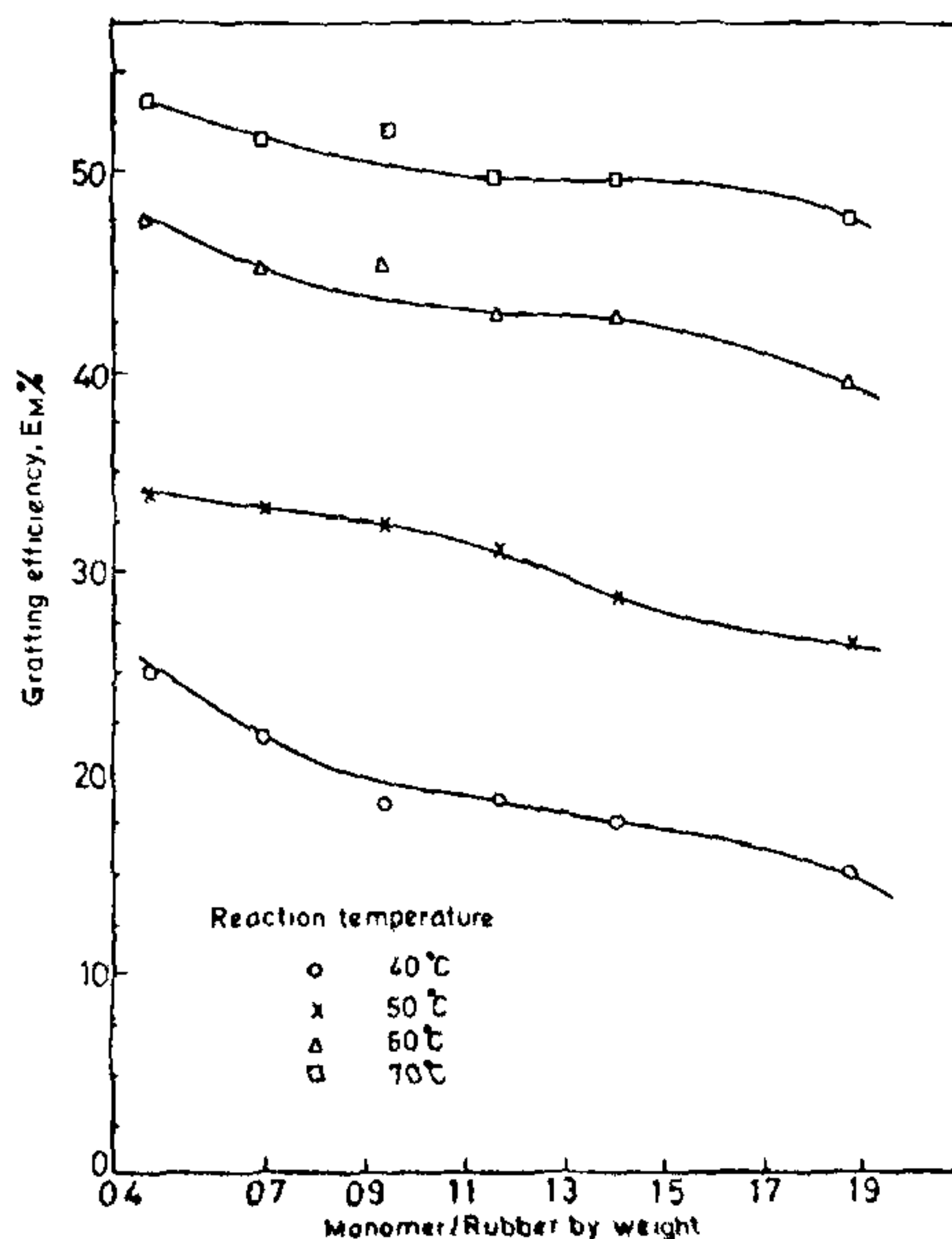


Figure 2. Relationship between percentage grafting efficiency E_M and ratio of monomer to rubber (by weight). Reaction time—6 hr, weight of rubber—2 g.

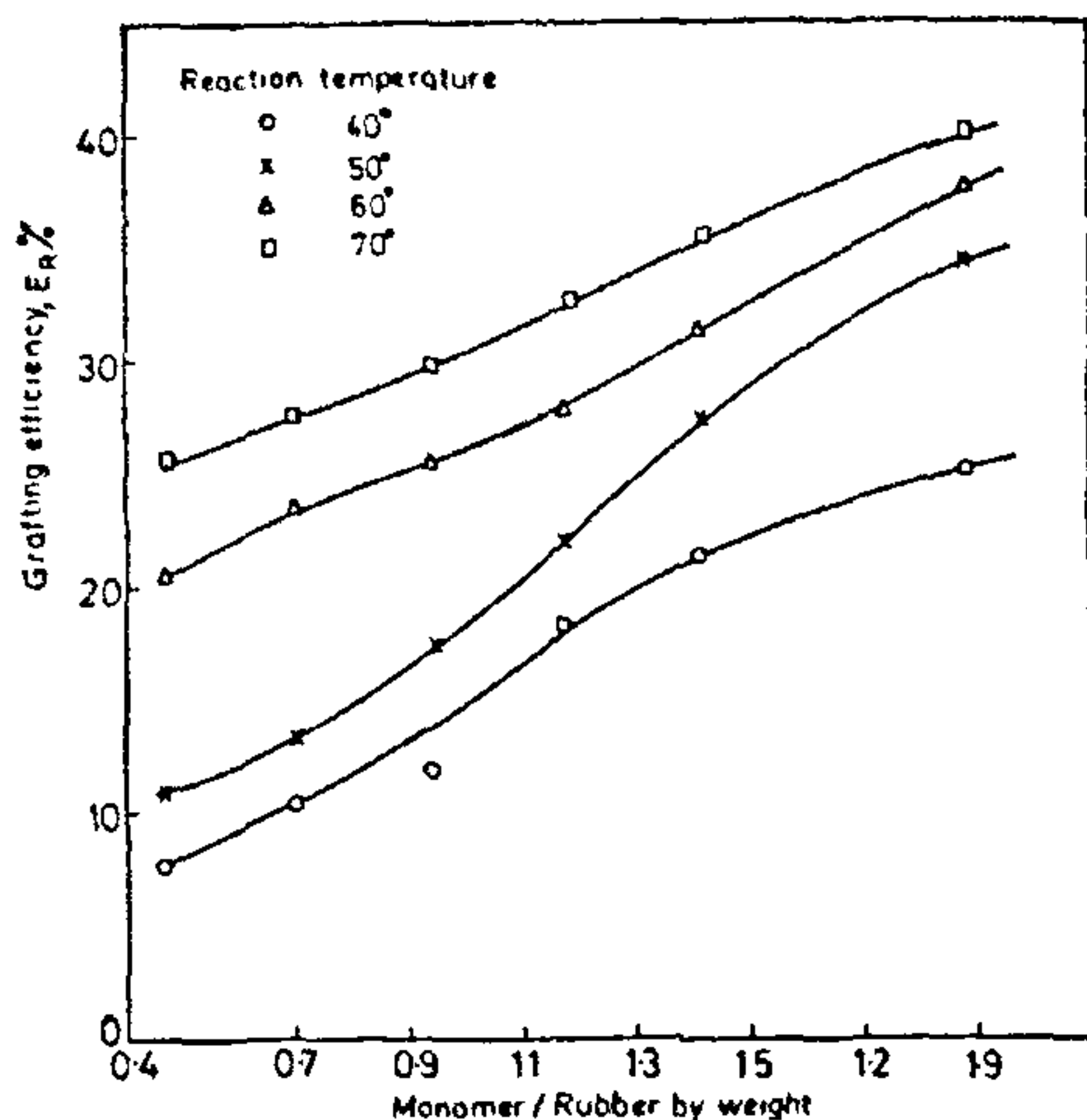


Figure 3. Relationship between percentage grafting efficiency E_R and ratio of monomer to rubber (by weight). Reaction time — 6 hr, weight of rubber — 2 g.

reaction temperature by 10°C to 60°C, increases E_M values by 12% (approx.), while there was an increase of only 6% (approx.) when temperature was increased from 60° to 70° C. At higher monomer concentration, increase of reaction temperature from 40° to 50° C increases E_R by 10% while further increase of 20° C gave only 5%. However, at low monomer concentration, the fast change in E_R was observed when the temperature was increased from 50° to 60° C. It was also observed that at any particular monomer concentration, temperature favours both the grafting efficiencies.

It has been reported earlier² that there is no copolymer formation of MMA and natural rubber in solution phase at 45° C. Our result clearly indicates that even at 40° C and under varied monomer

concentration, there is the formation of graft copolymer when copolymerisation is carried out in bulk phase. The grafted rubber was successfully isolated from the gross polymer, although the grafting efficiency (E_M or E_R) was much lower than that observed in equivalent experiments carried out at some higher temperature. It was also found in our experiments that the PMMA content in graft copolymer was maximum when the monomer to rubber ratio was 0.47.

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