

# Graft Characteristics and Solution Properties of Natural Rubber-*g*-Methyl Methacrylate Copolymer in MEK/Toluene

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## INTRODUCTION

Copolymers of natural rubber with methyl methacrylate styrene, acrylonitrile, and methacrylic acid have been reviewed by several authors.<sup>1-4</sup> The initiator systems employed include benzoyl peroxide,<sup>5-7</sup> redox systems,<sup>8</sup> and photochemical agencies.<sup>9-11</sup> The rubber samples used to prepare graft copolymers are solid, solution, or latex phases.<sup>5-7; 12-14</sup> The solid rubbers were masticated either in the presence of oxygen or in inert conditions. The copolymers prepared, irrespective of the monomers used, contained homopolymers and unreacted natural rubber. In the formation of natural rubber-*g*-methyl methacrylate copolymers, acetone is used selectively to extract free polymethyl methacrylate homopolymer while unreacted natural rubber is washed out with 60–80°C boiling point petroleum ether. Interest in the modification of natural rubber via copolymerization is to prepare a product that possesses some better properties than those of the unmodified natural rubber. Natural rubber-*g*-methyl methacrylate has been found useful as a shoe adhesive (trade name: Heaveaplus MG). A solvent mixture for such application is MEK/toluene. This study examines the dependence of grafting efficiency and graft level on the concentrations of methyl methacrylate and initiator and also the influence of the grafting characteristics on the hydrodynamics of the graft in MEK/toluene.

## MATERIALS

Methyl methacrylate, benzoyl peroxide, toluene, methyl ethyl ketone, and 60–80°C b.p. petroleum ether were all BDH products. Masticated crepe rubber crumb was obtained from ADC Nekede, Owerri, Nigeria.

## EXPERIMENTAL

Masticated crepe natural rubber crumb, 5–6 g, was dissolved in 88 cm<sup>3</sup> of redistilled toluene. Known weights of methyl methacrylate were added to it and the mixture was left for 4 h with occasional stirring before known volumes of 2% solution of benzoyl peroxide in toluene were added. Polymerization occurred under reflux at 80°C for 10 h under nitrogen atmosphere. The product coagulum was discharged into boiling water containing 5% formic acid. The product was washed with distilled water (×3) and dried in an oven at 50°C to a constant weight within 24 h.

Ungrafted natural rubber was washed out in a soxhlet extractor using 60–80°C boiling point petroleum ether for 24 h. The free rubber and residue were dried in a vacuum oven at 40°C for 24 h. Drying beyond 24 h did not alter the weight of the products. To free poly(methyl methacrylate) (PMMA) homopolymer, the residue was treated with acetone just as described when petroleum ether was used. The two products were then dried as before. There was no further weight loss after the 24 h drying time.

A Ubbelohde viscometer with a flow time of 105.46 s for a MEK/toluene (50 : 50 v/v) mixture was used for the hydrodynamic studies. Dissolution of the grafted copolymer was carried out in the solvent mixture at 35°C for 36 h. Measurement for intrinsic viscosity was made at 28 ± 0.05°C.

## RESULTS AND DISCUSSION

Table I shows the effect of initiator at a constant concentration of the monomer on the graft level and grafting efficiency. The grafting efficiency is calculated as the ratio of the amount of the graft copolymer to the amount of the product coagulum. The graft level is calculated as the ratio of the amount of graft copolymer to the amount of rubber grafted. As the concentration of the benzoyl peroxide increased, homopolymerization of methyl methacry-

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**Table I Graft Characteristics and Solution Properties of Natural Rubber-*g*-Methyl Methacrylate (Methyl Methacrylate = 0.10 Mol)**

| Sample | Concentration of Benzoyl Peroxide (mol $\times 10^5$ cm) | Wt of Product Coagulum (g) | Free Rubber (g) | Free PMMA (g) | Graft Copolymer (g) | Graft Level (%) | Grafting Efficiency (%) | $\eta$ (dL/g) | $K_H$ | $K_K$ |
|--------|--|----------------------------|-----------------|---------------|---------------------|-----------------|-------------------------|---------------|-------|-------|
| A      | 4.237  | 4.890                      | 0.511           | 0.893         | 3.486               | 77.66           | 71.29                   | 0.302         | 0.392 | 0.127 |
| B      | 8.474  | 5.00                       | 0.439           | 1.078         | 3.495               | 76.63           | 69.90                   | 0.288         | 0.362 | 0.152 |
| C      | 12.711   | 4.875                      | 0.430           | 1.072         | 3.430               | 75.05           | 70.36                   | 0.274         | 0.416 | 0.128 |
| D      | 16.948   | 4.914                      | 0.385           | 1.085         | 3.446               | 74.67           | 70.13                   | 0.222         | 0.341 | 0.183 |
| E      | 21.185   | 4.903                      | 0.303           | 1.086         | 3.514               | 74.81           | 70.28                   | 0.202         | .245  | .160  |

late increased initially but assumed a constant value when benzoyl peroxide concentration was equal to  $10 \times 10^{-5}$  mol/cm<sup>3</sup>. The free rubber concentration fell because of the formation of rubber radicals (Fig. 1). There was, thus, an increased rate of chain termination for formation of shorter grafts. With an increase in the concentration of the initiator, the values of intrinsic viscosity decreased with a cor-

responding decrease in the molecular weight of the graft copolymer. The graft level and the grafting efficiency decreased to a constant value as in Figure 2. As the monomer concentration increased, the amount of homopolymer (PMMA) increased, as in Figure 1(b). This means that homopolymerization was preferred to graft copolymerization. There were no new active sites on the rubber molecule, and at

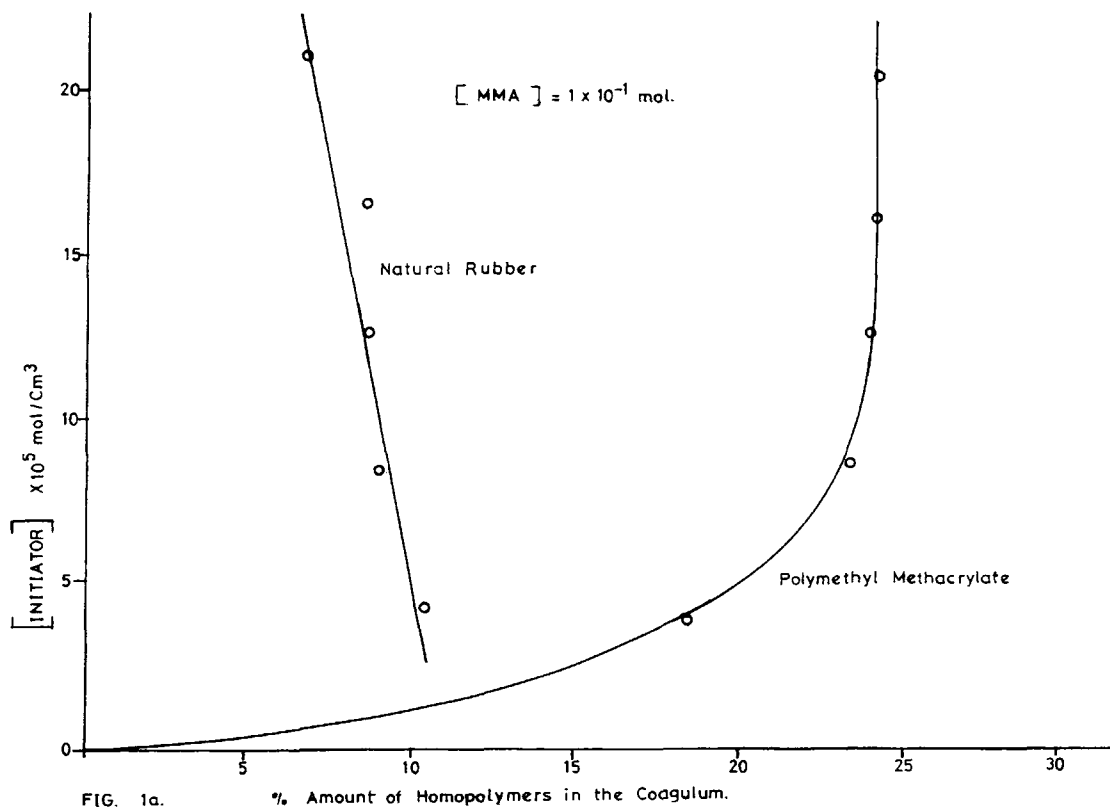


FIG. 1a. % Amount of Homopolymers in the Coagulum.

**Figure 1** (a) Effect of initiator concentration on homopolymers in natural rubber-*g*-methyl methacrylate formation at given monomer concentration. (b) Effect of monomer concentration on homopolymers in natural rubber-*g*-methyl methacrylate formation at given initiator concentration.

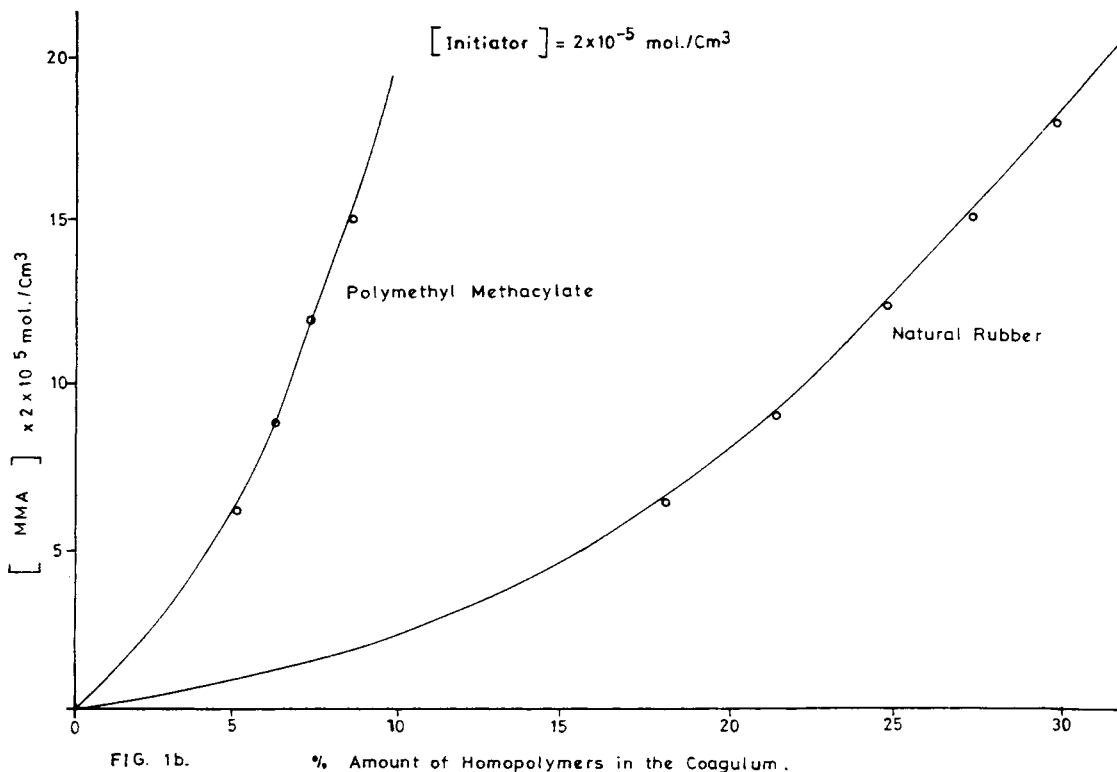


FIG. 1b. % Amount of Homopolymers in the Coagulum.

Figure 1 (Continued from the previous page)

a constant initiator concentration of  $2.5 \times 10^{-5} \text{ mol/cm}^3$ , both the graft level and the grafting efficiency decreased, as shown in Figure 3, with an increase in the concentration of the monomer.

The graft length increased and a rise in molecular weight was expected as seen in the values of the intrinsic viscosity in Table II. The intrinsic viscosities have been evaluated from Huggins and Kraemer

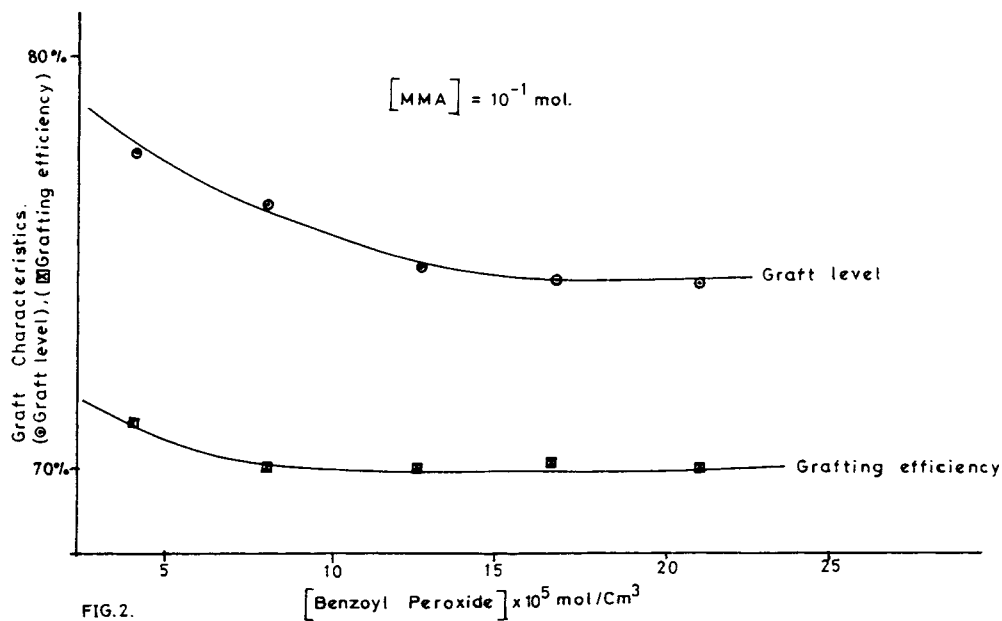


FIG. 2.

Figure 2 Graft characteristics (graft level and grafting efficiency) vs. initiator concentration at given monomer concentration.

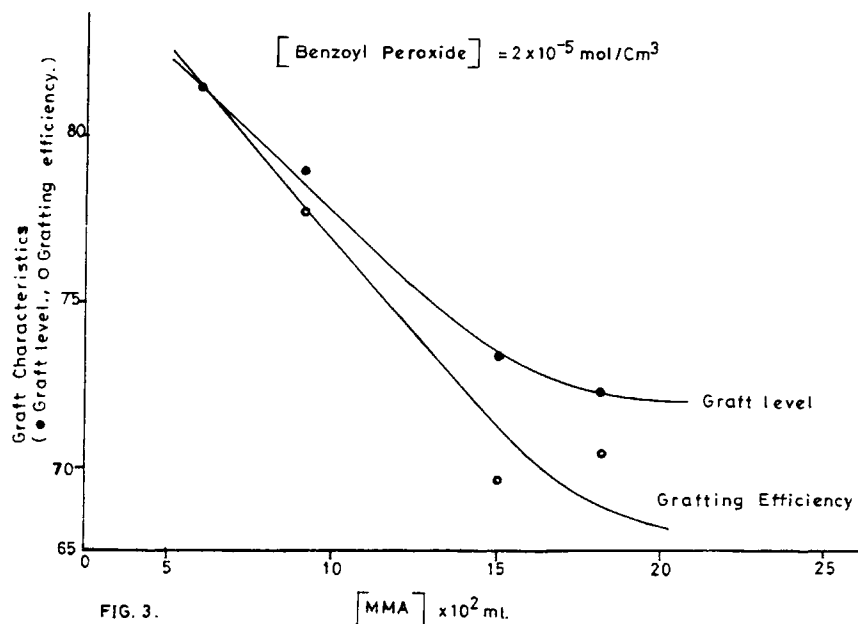


FIG. 3. Graft characteristics (graft level and grafting efficiency) at monomer concentration at given initiator concentration.

plots as a means of ascertaining the hydrodynamic behavior of the molecules of the graft under the conditions of the reaction. The difference between the slope constants  $K_H$  and  $K_k$  from the respective plots averaged to  $0.515 \pm 0.005$  as opposed to a value of 0.500 for homopolymers in which the free drainage model is applied. The small 3% deviation from 0.5 (3%) indicates dilute solution theories can be applied to the system investigated. Both MEK and toluene are good solvents for the natural rubber and for PMMA. This solvent mixture is useful in the formulation of this copolymer for use as adhesives for shoes.<sup>4</sup> A 50 : 50 ratio of the solvents will not adversely affect the hydrodynamic behavior of the graft copolymer when used to dissolve the graft for shoe applications.

## CONCLUSION

Despite the long period (25–30 years) of accumulation of research results, in natural rubber-*g*-methyl methacrylate, technological applications demand a correlation between grafting efficiency and graft level on the one hand, and the attendant influence on the hydrodynamics of the graft in technologically useful solvent mixture of MEK/toluene on the other hand. An increase in the concentration of methyl methacrylate at a given benzoyl peroxide initiator decreases both the graft level and grafting efficiency but increases the molecular weight of the copolymer. But an increase in the concentration of the benzoyl peroxide initiator at a given monomer concentration

Table II Graft Characteristics and Solution Properties of Rubber-*g*-Methyl Methacrylate, at (Initiator) =  $2 \times 10^{-5}$

| Sample | (MMA) ( $\times 10^2$ mole) | Wt of Product Coagulum | Free NR (3) | Free PMMA (3) | Graft Copolymer (g) | Graft Level (%) | Grafting Efficiency (%) | $\eta$ (dL/g) | $K_H$ | $K_K$ |
|--------|-----------------------------|------------------------|-------------|---------------|---------------------|-----------------|-------------------------|---------------|-------|-------|
| F      | 6                           | 5.700                  | 0.300       | 1.029         | 4.371               | 76.68           | 76.68                   | 0.233         | 0.350 | 0.178 |
| G      | 9                           | 5.776                  | 0.344       | 1.230         | 4.202               | 74.29           | 72.75                   | 0.242         | 0.285 | 0.213 |
| H      | 12                          | 6.012                  | 0.439       | 1.078         | 4.495               | 81.45           | 74.77                   | 0.288         | 0.365 | 0.152 |
| J      | 15                          | 5.845                  | 0.479       | 1.591         | 3.775               | 68.38           | 64.59                   | 0.327         | 0.334 | 0.123 |
| K      | 18                          | 5.899                  | 0.310       | 1.736         | 3.853               | 67.77           | 65.31                   | 0.422         | 0.358 | 0.190 |

decreases the graft level to a constant level when the benzoyl peroxide concentration exceeds approx.  $10 \times 10^{-2}$  mol/cm<sup>3</sup>. Dilute solution theory applicable to homopolymers can also be applied to the graft copolymers without any adverse effect in technological application.

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