



Graft copolymerization of vinyl acetate on gum Arabic using benzoyl peroxide. Effect of monomer concentration

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ABSTRACT

The graft copolymerization of vinyl acetate on gum Arabic was studied in the presence of benzoyl peroxide. The effect of monomer concentration over the range 1.62 – 9.76mol/L was investigated. It was found that the graft level increased steadily but the grafting efficiency decreased gradually. At 9.76mol/L monomer concentration, the graft level was 123.50% with grafting efficiency of 54.60% as compared to a graft level of 108.50% at 1.62mol/L with grafting efficiency of 65.35%. This indicates an increase in the graft level over the monomer concentration range.

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KEYWORDS

Copolymerization;
Gum Arabic;
Grafting;
Vinyl acetate;
Monomer.

INTRODUCTION

Graft copolymerization provides a unique technique for modifying polymers to meet desired use requirements. Graft copolymers of polysaccharides are of additional interest because of their potentials as enhanced viscosifiers in secondary petroleum recovery processes, and as flocculants in mining and wastewater treatments^[1]. Graft copolymerization of vinyl monomers is one of the universal effective and accessible methods for the chemical modification of natural polymers^[2].

An important advantage of graft copolymerization is that the polymeric substrate or backbone polymer and the grafted polymer chains are held together by chemical bonding allowing the two polymers to be intimately associated rather than as mere physical mixture. Thermodynamically, the grafted chains are expected to be distributed on the backbone polymer and impact

beneficial effects on the properties of the composite. Infact, the chemical, physical, mechanical and rheological properties of graft polymers correlate well with the size and distribution pattern of the grafted backbone polymer^[3]. Thus a major focus in graft copolymerization studies is the optimization of grafting frequency i.e. the number of polymer grafts introduced on the backbone polymer^[3].

Graft copolymers are becoming more important as an alternative to totally new linear polymers and copolymers, as the ability to synthesize polymers of any quality from readily available and reasonably in-expensive monomers is very attractive industrially^[4].

Grafting yield copolymers with remarkable changes in physiochemical properties with industrial and commercial values^[5-12].

Gum Arabic which is essentially a complex polysaccharide is a natural gum made of hardened sap taken

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from species of the acacia tree. It is harvested commercially throughout the sahel from Senegal and Sudan to Somalia and also in the northern part of Nigeria^[13]. Gum Arabic is useful as hydrocolloid, emulsifier, texturizer and film-former^[14].

Studies on graft copolymerization of vinyl acetate on gum Arabic by benzoyl peroxide is presented in this work. The effect of monomer concentration on the graft level and grafting efficiency was investigated and discussed.

EXPERIMENTAL

Gum Arabic was purchased from Kano market in Kano. It was purified by dissolving in deionized water for three days, filtered and precipitated in excess isopropanol and dried in vacuum.

Vinyl acetate monomer and benzoyl peroxide were obtained from Qualikems fine chemicals Ltd. All other reagents, that is, isopropanol (sigma aldrich inc.), methanol (sigma aldrich inc.), polyvinyl alcohol (BDH Ltd), acetic acid (BDH Ltd), sulphuric acid (sigma aldrich inc.), hydrochloric acid (BDH Ltd) and sodium hydroxide (chemproha chemical) were used as supplied.

GRAFTING PROCEDURE

The effect of monomer concentration was determined using various amounts of vinyl acetate and constant amounts of benzoyl peroxide and polyvinyl alcohol and the gum Arabic (2g) dispersed in 20ml of deionised water. The required amount of polyvinyl alcohol (4.53mol/L) was added to the beaker containing gum arabic and water. The required amount of benzoyl peroxide (0.02M) was introduced into a test tube containing vinyl acetate (1.62, 3.25, 4.88, 6.51, 8.13, and 9.76mol/L) respectively for the different sets of the experiment and in each case the reaction was allowed to proceed for 30mins in a water bath at a temperature 70°C. The benzoyl peroxide/vinyl acetate was then added to the beaker containing gum Arabic/ polyvinyl alcohol at 70°C and the polymerization reaction was allowed to proceed with agitation for 2hrs. The reaction mixture was poured into excess isopropanol (150 cm³) to precipitate the total polymer. It was filtered and dried in air.

The ungrafted polyvinyl acetate homopolymer formed was extracted with 1:1 acetic acid and water. The residue obtained was air-dried and weighed. The weight of the homopolymer was therefore reported as weight of total polymer minus weight of grafted polymer and weight of gum Arabic.

The percentage graft level, P_g, is reported as the weight of the grafted polymer, divided by the weight of the gum Arabic used multiplied by 100,^[15].

$$\% P_g = \frac{W_2}{W_1} \times 100$$

Where W₁ and W₂ are the weight of the gum Arabic and grafted polymer respectively.

The grafting efficiency, P_e, is reported as weight of grafted polymer divided by the weight of synthesized polymer formed (weight of grafted polymer and weight of homopolymer) multiplied by 100,^[15].

$$\% P_g = \frac{W_2}{W_1} \times 100$$

ISOLATION AND MOLECULAR WEIGHT DETERMINATION OF GRAFTED POLYMER CHAINS

The grafted polymer chains were isolated from the backbone polymer by treatment with 5ml dilute sulphuric acid for 24 hours at room temperature. The mixture was poured into excess methanol (100cm³) and the grafted polymer precipitated was dried overnight. The isolated polymer was dissolved in acetone and the average molecular weight was determined from viscosity measurement in acetone at 25°C using Mark-Houwink equation.

$$\eta = KMv^a$$

where η is the intrinsic viscosity of the polymer, Mv

TABLE 1 : Variation of vinyl acetate (monomer) concentration

| Benzoyl peroxide (M) | % graft level | Grafting efficiency (%) | Mv of grafted chains 10 ⁻³ |
|----------------------|---------------|-------------------------|---------------------------------------|
| 0.02 | 120.5 | 54.64 | 27.2 |
| 0.04 | 123.5 | 57.14 | 20.9 |
| 0.06 | 120.0 | 58.47 | 19.8 |
| 0.08 | 112.5 | 60.24 | 12.3 |
| 0.10 | 111.0 | 59.52 | 13.9 |
| 0.12 | 110.0 | 52.91 | 11.3 |

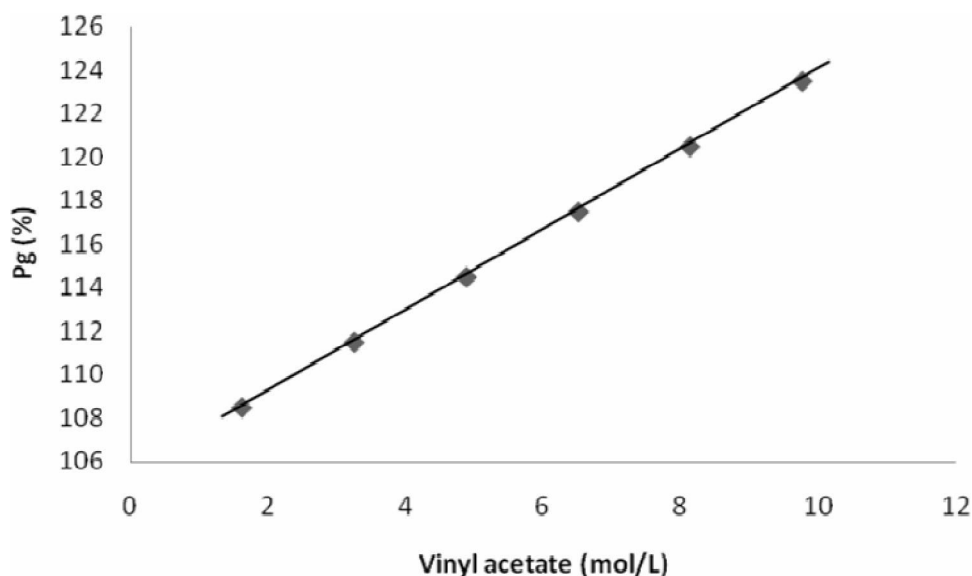


Figure 1 : Effect of vinyl acetate concentration on % graft level

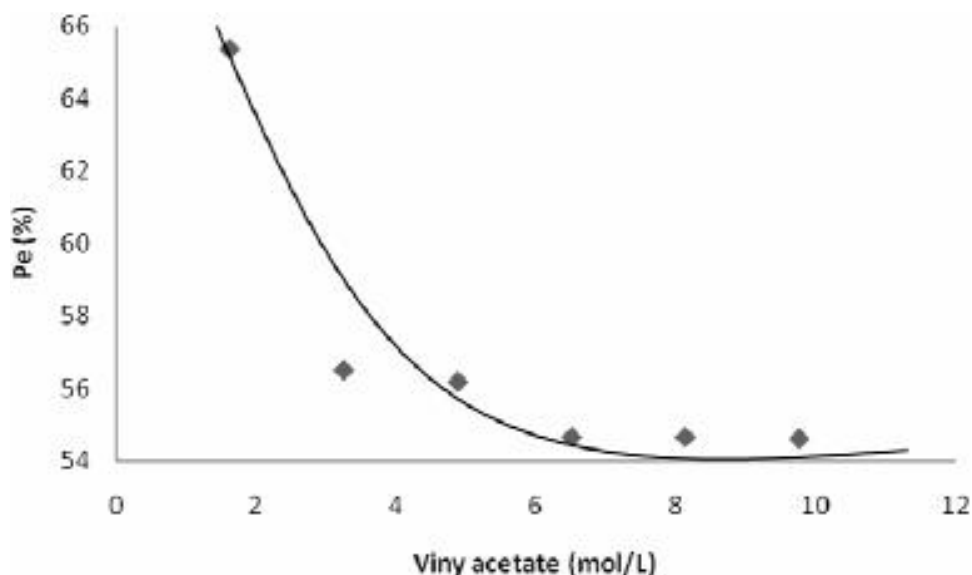


Figure 2 : Effect of vinyl acetate concentration on grafting efficiency

is the average molecular weight, K and a are empirical (Mark - Houwink) constants that are specific for a given polymer, solvent and temperature.

RESULTS AND DISCUSSION

The graft level increased steadily with monomer concentration over the range 1.62-9.76mol/L as can be seen in Figure 1.

This is consistent with the findings of Das, Noyak and Singh (1991) and Eromosele and Hamagudu (1993) and the extent of grafting depended on the amount of vinyl acetate. It is suggested that the increase in graft

level may be attributed to gel effect and enhanced solubility of polyvinyl acetate in its monomer and its rate of diffusion into the gum Arabic matrix^[4].

The grafting efficiency decreased gradually with increase in monomer concentration as shown in Figure 2.

According to Okiemen and Idehen (1987), in a polymerization system containing fixed amount of initiator, water and cellulose, there would be a maximum amount of the monomer that would be complexed. An increase in the monomer concentration above the maximum value would not be expected to result in an increase in the extent of graft copolymer formation.

The average molecular weight of the grafted gum

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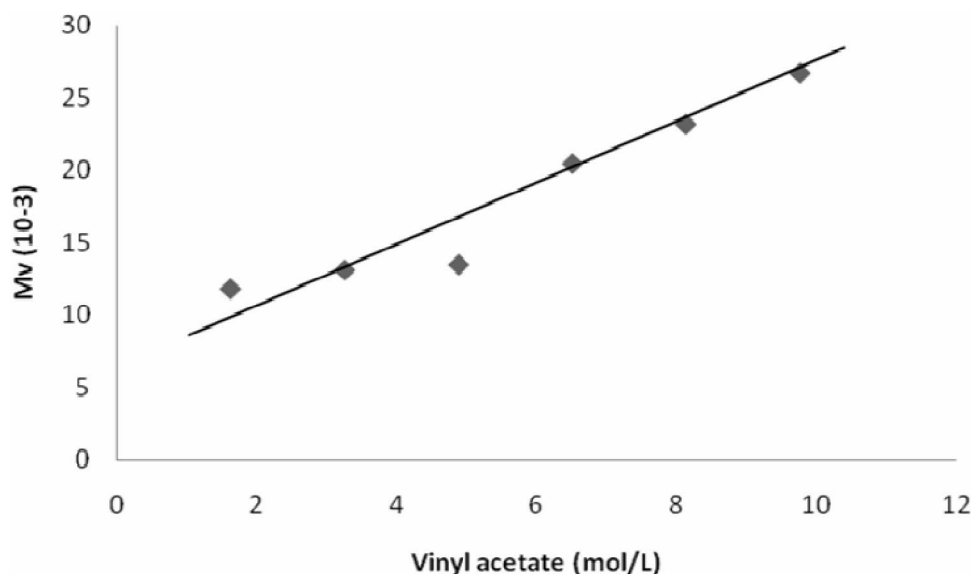


Figure 3 : Effect of vinyl acetate concentration on the average molecular weight of grafted chains.

Arabic increases with increase in monomer concentration as shown in Figure 3.

The result of this findings is consistent with the work of Bazuaye, Okiemen and Said (1998). The increase in molecular weight may be due to enhanced utilization of more grafting site on the gum Arabic, monomer solubility and its rate of diffusion into the gum matrix.

CONCLUSION

The graft copolymerization of vinyl acetate on gum Arabic using benzoyl peroxide was presented in this article. Benzoyl peroxide can successfully initiate graft copolymerization of vinyl acetate onto gum Arabic. The effect of monomer concentration was investigated and discussed. It was found that the graft level increased slowly with increased monomer concentration, but the grafting efficiency decreased gradually. The increase in graft level may be attributed to gel effect and enhanced solubility of polyvinyl acetate in its monomer, and its rate of diffusion into the gum matrix.

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