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Graft copolymerization of vinyl acetate on gum Arabic

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ABSTRACT

Graft copolymerization of vinyl acetate onto gum Arabic obtained from Kano market, Kano Nigeria was achieved using benzoyl peroxide initiator at 70°C. The highest graft level was obtained at 0.04M benzoyl peroxide concentration. The graft copolymers were characterized in terms of graft level, grafting efficiency and molecular weight of the grafted chains. The grafted copolymer samples were used to produce adhesives. It was found that the grafted copolymer adhesives were more efficient than adhesive made of ungrafted gum Arabic.

KEYWORDS

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

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 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].

Benzoyl peroxide is often used in homopolymerization especially in suspension and emulsion polymerization. In this work, Benzoyl peroxide initiated graft copolymerization was investigated in order to establish the conditions under which successful graft copolymerization can occur.

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

2g of gum Arabic was dispersed in 20ml of deionised water in a beaker overnight, 1.51mol/L of polyvinyl alcohol was added and the beaker was placed in a water bath and heated at a temperature of 70°C. 4.88mol/L of vinyl acetate was placed in a test tube, a known amount of benzoyl peroxide (0.02M, 0.04M, 0.06M, 0.08M, 0.10M, and 0.12M) respectively for the different sets of the experiment was added and heated at a temperature of 70°C in a water bath for 30mins to allow for dissociation and interaction of benzoyl peroxide with the vinyl acetate. The benzoyl peroxide/vinyl acetate was then added to the beaker containing gum Arabic/polyvinyl alcohol at 70°C. The polymerization reaction was allowed to proceed with agitation for about 2hrs. The reaction mixture was poured into excess isopropanol (150 cm^3) 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, Pg, is reported as the weight of the grafted polymer, divided by the weight of the gum Arabic used multiplied by 100[15].

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

Where W_1 and W_2 are the weight of the gum Arabic and grafted polymer respectively.

The grafting efficiency, Pe, 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].

$$\%\ Pe = \frac{W_2}{W_2 + W_3} \times 100$$

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 (100cm^3) 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 is the average molecular weight, K and a are empirical (Mark - Houwink) constants that are specific for a given polymer, solvent and temperature.

Production of adhesive

10% of the gum Arabic-g-vinyl acetate was prepared by dissolving 3g of the copolymer in 7mls of water. The sample was then stabilized with 0.2g of formalin and 0.5g of glycerine. Formalin prevents the growth of micro-organisms in the adhesive thus stabilize the adhesive against degradation. Glycerine is a humectant (moisturizer), it helps to prevent complete dryness in the adhesive fluid.

The properties of the adhesive i.e pH, viscosity and density were measured using the Jenway 3510 pH meter, viscometer and density bottle respectively.

Other tests were carried out on the adhesive to assess the bond strength and service performance of the adhesive. These tests include; Drying time, Bond

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strength, Peel strength, Heat resistance, and Moisture resistance[16].

RESULTS AND DISCUSSION

The graft level of vinyl acetate on gum Arabic with benzoyl peroxide initiator is shown in Figure 1.

Pg (%) increases in value and attained a maximum at 0.04M concentration of benzoyl peroxide. This indicates that the benzoyl peroxide exclusively participate in the formation of active sites on the substrate and beyond it no more active sites are formed on the gum Arabic. Further increase in benzoyl peroxide concentration is accompanied by decrease in percentage graft levels. The levels obtained are higher especially at lower benzoyl peroxide concentration. The high graft yield may also be attributed to gel effect caused by the polyvinyl alcohol and enhanced solubility of vinyl acetate in the polymerization medium.

TABLE 1 : Variation of benzoyl peroxide initiator 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

The grafting efficiency of vinyl acetate on gum Arabic with benzoyl peroxide initiator is shown in Figure 2.

Maximum grafting efficiency, (60.24%) was attained at about 0.08M Benzoyl peroxide concentration. Beyond this concentration %Pe decreases. It is generally well recognized that the physical state of the polymerization medium is an important factor affecting the extent of graft polymer formation. According to Mc Dowall et al. (1984), the extent of grafting would depend on the monomer type, the electronic charge and the reactivity of the monomer towards the graft polymer formation. Since efficiency measures the degree of effectiveness of grafting, the results showed that a good percentage of vinyl acetate in the copolymer was grafted onto the gum Arabic.

The average molecular weight of the grafted polymer chains is shown in Figure 3.

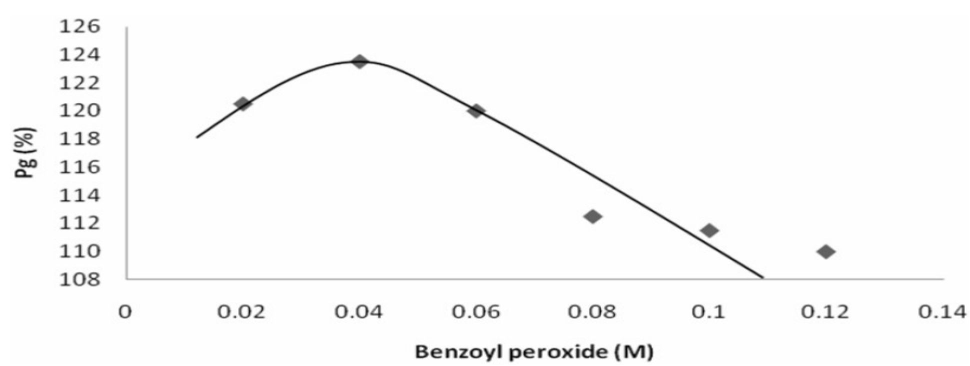

Figure 1 : Effect of benzoyl peroxide concentration on % graft level

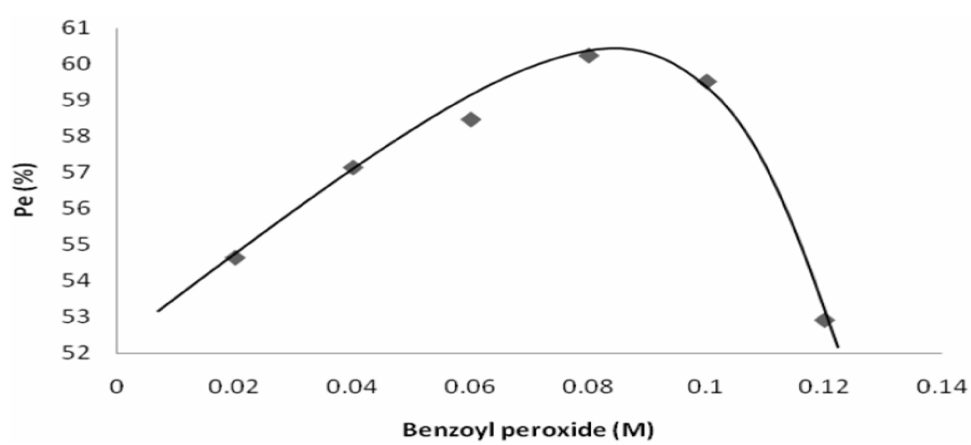

Figure 2 : Effect of benzoyl peroxide concentration on grafting efficiency

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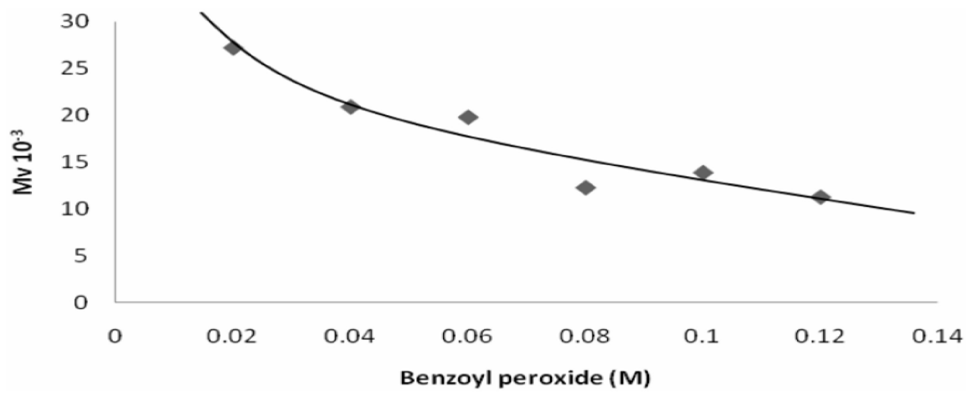

Figure 3 : Effect of benzoyl peroxide concentration on the average molecular weight of grafted chains

The molecular weight of the grafted polymer chains decreases with increasing benzoyl peroxide concentration. It is observed that increase in molecular weight is more enhanced while using smaller concentrations of benzoyl peroxide. Though the vinyl acetate was soluble in the polymerization medium, the decrease in molecular weight may be due to the slow rate of diffusion of the vinyl acetate into the gum Arabic matrix, indicating an underutilization of more grafting site on the gum Arabic.

Evaluation of graft copolymers as adhesives

Laboratory tests were run on two graft copolymer samples with Pg 120.5% and 123.5% to obtain some estimate of gum Arabic-polyvinyl acetate graft copolymers as adhesives. The characteristics of the copolymer samples used in the adhesive tests are given in TABLE 2.

TABLE 2 : Characteristics of the gum Arabic graft copolymer used in the adhesive tests

Gum Arabic-polyvinyl acetate copolymer sample	Graft level (%)	Molecular wt. of grafted polymer 10^{-3} Mv	Grafting Efficiency (%)
A	120.5	27.20	54.64
B	123.5	20.90	57.14

Various property tests were carried out on the raw gum Arabic and the copolymer samples. The results obtained were compared with adhesive made of ungrafted gum Arabic.

TABLES 5-8 compares the efficiency of two graft copolymers and gum Arabic as adhesives. It is clear that the graft copolymers are better adhesives than the ungrafted gum Arabic in paper application. This indicates that a graft copolymer is more efficient as adhesive than the natural polymer. The pH of the copolymer adhesives falls within the range of the pH of raw gum Arabic and they gave satisfactory viscosities. While it took the ungrafted gum Arabic adhesive 6hrs to cure, it took the copolymer adhesives 1hr to cure. This is because polyvinyl acetate is a fast binding adhesive. The copolymer adhesives have a higher bond strength and moisture resistance than ungrafted gum Arabic adhesive. This is as a result of the fact that polyvinyl acetate is capable of forming strong bond and it has a high resistance to moisture absorption[17]. Also, the copolymer adhesives have a higher resistance to heat compared to ungrafted gum Arabic adhesive, this is owed to polyvinyl acetate which has great stability to heat and light[18].

TABLE 3 : Measurement of pH, density and viscosity of raw gum, copolymer samples and ungrafted gum adhesive.

Sample	pH	Density (g/ml)	Viscosity (Ns/m^2)
Raw gum	4.77	1.05	4.82
A	4.28	1.06	4.52
B	4.84	1.07	4.92
C	4.24	1.06	4.50

Where sample C is adhesive made of ungrafted gum Arabic.

TABLE 4 : Drying time tests

Time taken	Sample A	Sample B	Sample C
30mins	Very good	Very good	Poor
1hr	Excellent	Excellent	Fair
2hrs	-	-	Fair
3hrs	-	-	Good
4hrs	-	-	Good
5hrs	-	-	Very good
6hrs	-	-	Excellent

TABLE 5 : Bond strength tests

Force (N)	Standard time (hr)	Observed time of failure (mins)	Sample A	Sample B	Sample C
10	12	30	No failure	No failure	Failure observed
20	12	-	No failure	No failure	-

TABLE 6 : Peel strength tests

Force (N)	Standard time (hr)	Observed time of failure (mins)	Sample A	Sample B	Sample C
10	12	10	No tearing observed	No tearing observed	Tearing observed
15	12	480	Tearing observed	Tearing observed	-

TABLE 7 : Heat resistance tests

Force (N)	Standard time (hr)	Observed time of failure (hr)	Sample A	Sample B	Sample C
10	12	3	No failure	No failure	Failure observed
20	12	-	No failure	No failure	-

TABLE 8 : Moisture resistance tests

Force (N)	Standard time (hr)	Observed time of failure (mins)	Sample A	Sample B	Sample C
10	12	5	No failure	No failure	Failure observed
20	12	360	Failure observed	Failure observed	-

CONCLUSION

Benzoyl peroxide can successfully initiate graft copolymerization of vinyl acetate onto gum Arabic. The results from this research have provided further information on the mechanism of graft polymer formation.

Gum Arabic have been modified by grafting vinyl acetate onto it. Some of the properties that are modified include, heat resistance and moisture absorption. The graft copolymers show better efficiency as adhesives. The enhanced efficiency of the gum Arabic-g-vinyl acetate is suggested to be due to its greater degree of branching and higher molecular weight as well as the polyvinyl acetates ability to dry on time, form strong bond, resist heat and moisture absorption. The copolymer adhesive can be used for paper to paper bonding for example in bookbinding, envelopes and stamps.

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