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SYNTHESIS OF WATER SOLUBLE POLYMER BASED ON ACRYLIC ACID AND ACRYLAMIDE BY INVERSE SUSPENSION METHOD

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ABSTRACT

The copolymerization of acrylic acid (AA) and acrylamide (AM) using ammonium persulfate as initiator was studied by inverse suspension method. Effect of reaction temperature, time and initiator concentration on the average molecular weight was studied in detail. The optimal reaction conditions for the above parameters are 76 ^{o}C, 120 min and 1.0 % correspondingly. Morphology of the reaction products was also characterized by scanning electron microscope (SEM).

Từ khóa: copolymer, acrylamide, acrylic acid, inverse suspension.

1. INTRODUCTION

Hydrophilic polymers are used in many different industries depending on the composition of the monomer. Water-soluble polymers synthesized based on acrylic acid and acrylamide account for a very large share of applications in life such as: water treatment, paper processing, mineral processing, industrial textiles, footwear, cosmetics, pharmaceutical, oil recovery, and especially in agriculture [1 - 5]. There are many methods to synthesize hydrophilic polymers, in which the inverse suspension method has been applied in several industries [6].

In this paper, copolymers of acrylic acid and acrylamide (PAAM) was synthesized by inverse suspension polymerization method, some factors such as reaction temperature, time and concentration of initiator affecting on the polymerization of acrylic acid and acrylamide were studied.

2. EXPERIMENTAL

2.1. Material

Acrylamide (AM)> 99% (China), acrylic acid (AA)> 99% (China), $(NH_4)_2S_2O_8$ (APS), methanol, dioxane (China), span 80 ($C_{24}H_{44}O_6$) (China): M = 428.61 g/mol, HLB = 4.3; liquid paraffin: density of 0.845 g/ml, flash temperature > 180 ^oC, cyclohexane solvent (C_6H_{12}) (China): M = 84.16 g/mol, density of 0.779 g/ml, 84.74 °C boiling point, distilled water.

2.2. Synthesis of copolymer

The process of inverse suspension polymerization was carried out in a steel flask with 1000 ml, three neck connected with agitator, temperature controller (water bath), reflux device, path tube of aeration nitrogen and drip funnel.

Mixture of liquid paraffin with span 80 surfactant (a ratio of span 80/paraffin = 0.33% and a ratio of monomers/solvent = 1/4) was poured into the flask and heated to the reaction temperature. Initiator was added to mixture of monomers (mixture included acrylamide and acrylic acid with different monomer ratios). After then this solution was dropped into the flask by separator funnel at speed of 10 g/min, maintaining the stirring at 300 rpm/min in nitrogen. When fully loaded monomers, the rate of stirring and the reaction temperature were kept unchanged. Finally, the reaction mixture was cooled down to room temperature while stirring. After filtering, polymer was washed several times with cyclohexane to remove paraffin liquid.

The reaction products included: poly(AA-co-AM), homopolymer of monomers (polyacrylic acid (PAA), polyacrylamide (PAM)) and residual monomers. Firstly, product mixture was dissolved in methanol to remove residual monomers. Then, soxhlet extraction was done in dioxane solution at 4 hours to remove PAA. Finally, the mixture of poly(AA-co-AM), PAM were distilled in methanol-water solution (50/50v/v) to remove PAM. The poly (AA-co-AM) solution in methanol-water was precipitated in pure methanol solution to precipitate. Finally extracted copolymer was dried in oven at 70 °C to constant weight. Average molecular weight of the copolymer PAAM was determined by measurement of viscosity on Ubbelohde viscometer at 30 ° C in water. Average molecular weight of PAAM was calculated using Mark-Houwink equation:

$$[\eta]_{H2O} = 3{,}66 \times 10^{-2}\left(\frac{M_\eta}{71}\right)^{0{,}66}$$

The average size of the particles was determined relatively from SEM images of copolymer as the following:

$$\overline{D_n} = \frac{\sum_{i=0}^{N} D_i}{N}$$

where: N is the total number of particles that displayed on the SEM image integrity, D_i is the size of the i^{th} particle.

3. RESULTS AND DISCUSSION

The optimal conditions obtained from the copolymerization in dilute solution were: reaction temperature of 71 °C, reaction time of ≈100 minutes, initiator concentration of 1.0 % (by weight amount of monomer) [7]. However, when applying these conditions to synthesize PAAM by inverse suspension method, the resulting product was not satisfactory, the polymer

seeds still attached to the block at the bottom of the device. This may be due to the reaction took place not completely, still partially unreacted out and make the adhesive. Therefore, factors such as reaction temperature, time and concentration of initiator are not optimal conditions of the inverse suspension method. These factors need to be studied further.

3.1. Influence of reaction temperature and time

In this study, the reaction was carried out in the following conditions: ratio of AA/AM = 50:50, monomer concentration of 25 %w/w, APS initiator concentration of 1.0 % (total monomer), stirring rate of 300 rpm/min, monomer/solvent paraffin ratio of 1/4, concentration of span 80 surfactant of 0.33 %, with various temperature and time. The results are shown in Table 1.

Table1. Effect of reaction time and temperature.

Temperature (^oC)	Time (min)	Product features	D_{TB} (μm)
71	100	Adhesive block	Unidentified
	110	Adhesive block	Unidentified
	120	Block stick particles	Unidentified
	150	Block stick particles	Unidentified
76	100	Granulation, still adhesive	Unidentified
	110	Create irregular particles	Unidentified
	120	Create regular particles	~80-110

Table 1 shows that at 71 °C, the products formed in the adhesive block with no particle formation. At 76 °C, the reaction time is less than 120 minutes, the particles formed without separation, but still stuck to the block - particles, the type of this product did not meet the requirements of a suspension polymerization product. This is due to time low and low temperature, the polymer obtained with low molecular weight could be dispersed in the solvent so it would be difficult to create a separate under stirring conditions.

With the reaction temperature of 76 °C and reaction time of 120 minutes, the particles were separated. This product meets the requirements. Thus the temperature of 76 °C was chosen as the study conditions for the next reaction.

3.2. Effect of initiator concentration and reaction time

In this research, the reaction was carried out in the conditions as: ratio of AA/AM = 50/50, ratio of monomer/solvent paraffin of 1/4, concentration of span 80 surfactant of 0.33 %, and the initiator concentration and reaction time were varyed. The results are presented in Table 2.

Table 2. Effect of initiator concentration and reaction time.

Time (min)	Initiator concentration (%)	Product Features	D_{TB} (μm)	KLPT (g/mol)
100	1.0	Adhesive block	-	-
	1.1	Adhesive block	-	-
	1.2	Graining, adhesive	-	-
110	1.0	Graining, adhesive	-	-
	1.1	Graining, adhesive	-	-
	1.2	Create regular particles	~80-110	$3,18.10^5$
	1.4	Create regular particles	~80-110	$2,78.10^5$
120	1.0	Create regular particles	~80-110	$3,87.10^5$
	1.1	Create regular particles	~80-110	$3,46.10^5$

The results indicated that optical conditions are reaction temperature of 76 °C, concentration of initiator of 1.0 % (total monomers) and reaction time of 120 minutes.

3.3. Molecular weight of the copolymer PAAM

Average molecular weight of the copolymer PAAM was determined by measurement of viscosity on Ubbelohde viscometer at 30 °C in water. The PAAM was completely dissolved in water to obtain a solution with a concentration of 0.025 to 0.3 g/100 ml. The chart for the relationship of η/C to C is shown in Figure 1.

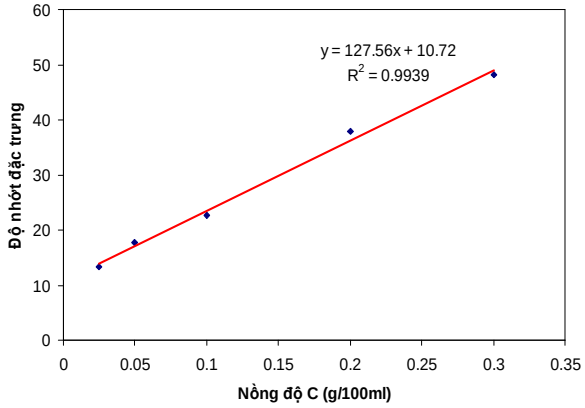
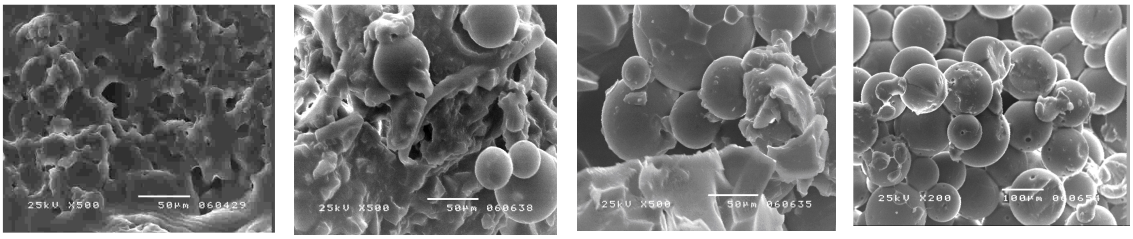


Figure 1. Relationship of η/C to C of PAAM.

The calculation results showed that the average molecular weight of the copolymer PAAM is: Mn = 387.214 g/mol ≈ $3.87.10^5$ g/mol.

3.4. SEM images of the PAAM

The SEM images of the PAAM are shown in Figure 2.



Samples at 71 ^{o}C for 110 minutes	Samples at 71 ^{o}C for 120 minutes	Samples at 71 ^{o}C for 150 minutes	Samples at 76 ^{o}C for 120 minutes

Figure 2. SEM image of the PAAM.

Figure 2 demonstrates the surface morphology of the particles as dependent on the temperature and at different times, which show that in the sample after 120 minutes and at a temperature of 76 °C, stirring 300 rounds/minutes, the particle's ability to created better products.

4. CONCLUSION

Copolymers of acrylic acid and acrylamide PAAM was synthesized by the method of inverse suspension polymerization in the presence of ammonium persulfate initiator. The best copolymers were obtained with molecular weights of 3.8×10^5 (g/mol) for the conditions following: temperature of 76 °C, initiator concentration of 1.0 % (total monomers), reaction time of 120 minutes, stirring speed of 300 rpm/min, ratio of span 80/paraffin = 0.33 and ratio of monomers/solvent = 1/4.

The research shows that inverse suspension method proceeds at high concentrations of monomers and the copolymers obtained with high molecular weight. Products obtained has a molecular weight in the average range, which meets requirements for applications in soil fixation and soil emaciation.

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TÓM TẮT

TỔNG HỢP POLYME ƯA NƯỚC TRÊN CƠ SỞ AXIT ACRYLIC VÀ ACRYLAMIT BẰNG PHƯƠNG PHÁP HUYỀN PHÙ NGƯỢC

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Quá trình đồng trùng hợp acrylamit (AM) và axit acrylic sử dụng chất khơi mào amoni pesunfat đã được nghiên cứu bằng phương pháp huyền phù ngược. Một số yếu tố ảnh hưởng như nồng độ chất khơi mào, nhiệt độ phản ứng đến khối lượng phân tử trung bình cũng được nghiên cứu. Các điều kiện tối ưu thu được là: nhiệt độ 76 ^{o}C, thời gian phản ứng 120 phút, nồng độ chất khơi mào 1 %. Hình thái học của sản phẩm được phân tích bởi kính hiển vi điện tử quét (SEM).

Từ khóa: polyme ưa nước, acrylamit, axit acrylic, huyền phù ngược.