

Synthesis and delayed germination of vinyl acetate-butyl acrylate copolymer for coating of sugar beet seeds using combined experimental design and image analysis

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Abstract

Seeds are coated widely with different polymers for increasing productivity and improving stand establishment of different crops. Emulsion copolymerization of vinyl acetate and butyl acrylate can be used for sugar beet seed coating. In this study, for the first time, a fractional factorial design, as a statistical experimental design method, was combined with image analysis method to achieve the optimal condition for emulsion copolymerization of vinyl acetate (VAc) and butyl acrylate (BuA) as a delayed-germination copolymer. The optimum condition was on the time of 3.16 hours, the temperature of 65°C, the initiator concentration and anionic surfactant of 0.0121 wt%. The synthesized copolymer was homogeneous and was characterized using ATR-Fourier transform infrared spectroscopy (ATR-FTIR), Differential Scanning Calorimetry (DSC), Particle Size Distribution (PSD) and Scanning Electron Microscope (SEM) analysis. Then the synthesized copolymer was used for coating of sugar beet seeds. The results show that the synthesized copolymer does not have adverse interaction with pesticides, fungicides and the color, which used for seed coating. Therefore, it can be used in coating of sugar beet seeds. Also, the synthesized copolymer delayed germination about 40 days.

Keywords: Vinyl acetate, Butyl acrylate, Delayed germination copolymer, Image analysis, Seed coating.

1. Introduction

Emulsion polymerization is extensively used to produce latexes with a great extended variety of properties, such as better adhesion, high resistance to freezing and thawing [1,2]. The properties of copolymer latexes depend on the copolymer composition, initiator, polymerization conditions, and

colloidal characteristics of the copolymer particles [3-5].

Polymer latexes of vinyl acetate (VAc) are widely used in industrial applications like adhesives, coatings, and paints, because of the physical characteristics of the films, low cost and availability [6]. Many researches carried out copolymers of VAc/BuA with a butyl

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acrylate (BuA) composition of 15–25 wt% as a one of the most important industrial latexes which is widely used in different applications [7,8]. One of these applications is seed coating, because this copolymer is a temperature-sensitive polymer.

Emulsion copolymerization of vinyl acetate (VAc) and butyl acrylate (BuA) in the coating industries was achieved to produce polymer latexes with controlled glass transition temperatures (T_g) [9]. In addition, the outstanding resistance to water, weathering, oxygen, and light, the excellent film formability and the adhesion performance, as well as low cost are the other advantages of vinyl acetate-butyl acrylate copolymer (VAc/BuA) emulsion [10,11]. The emulsion polymerization of VAc/BuA comonomers is complicated by the great difference in reactivity ratios and water solubilities of the two monomers [12,13].

Mattioni [14] showed that quantitative structure-property relationships (QSPR) are developed to correlate glass transition temperatures and chemical structure. The glass transition temperature (T_g) of the copolymer can be varied under a great range by changing the proportion between the two monomers [15,16]. Fox used an equation to estimate glass transition temperature [17].

In recent years, Seed coating with composites, which made from chemical materials is an efficient method to improve its germination [18,19]. Puglisi and Guth [20] synthesized composites with -60 to 20 °C T_g which can be used for seed coating under low temperature. This coating is resistant against pesticides and fungicides in the environment, scratching and scaling under lower temperatures than 20 °C. Schotterbeck [21] evaluated that the glass transition (T_g) between -30 to 30 °C, is useful for the seed of various cultivated plants, such as, sugar beet, wheat, barley, soybeans, and tomatoes.

Evaluation of seed coating on plant germination and establishment showed that in some cases, polymer coating caused seed germination delay. Intelligent polymers have the ability to be improved by organic and inorganic materials and are sensitive to any environmental changes [22,23]. Upedhyay [24]

evaluated the economic value of temperature-sensitive polymer coating usage for autumn rapeseed planting. Their results showed that early autumn planting of the seeds coated with temperature-sensitive polymer had a positive impact with higher net income compared with normal seeds. Seeds were coated with these polymers survive in the soil, tolerate frost and freezing, and protect the seed. When the soil temperature rises, the polymer cracks and seed is released together with essential additives and began to grow [25, 26].

The economic evaluation of sensitive polymer to temperature coating in Canadian regions with short growing seasons illustrated that applied polymer does not allow seed germination upon optimum germination temperature achieved. The base temperature for corn and soybean is 10 and 12 °C, respectively. According to the statistical-economic modeling results on the basis of planting on different dates, 61 and 97% of this type of temperature-sensitive polymer can be used for corn and soybean. This model can also be extended to other seed crops [27].

The quality of the polymer depends on their homogeneity which can be controlled by setting the level of important factors such as surfactant, initiator, time and temperature in the synthesis procedure. Therefore, the synthesis process demands an optimization method to achieve the experimental conditions where the polymer is synthesized completely homogenous.

Experimental design methods have been widely used to plan and analyze experiments, in order to extract the maximum amount of information with the fewest number of runs [28-30]. One-factor-at-a time (OFAT) is a traditional optimization method in which the effect of one factor at a time on an experimental response is monitored, thus it may trapped in a local optimum and miss the global optimum, because it ignores the interaction effects of the parameters among the factors studied. Therefore, this method does not depict the complete effects of the parameters on the response. Another disadvantage of this technique is the large number of experiments which is necessary to conduct

the research. Indeed, it requires a lot of resources such as material and reagent and time. On the contrary, experimental design methods allow changing simultaneously all variables, helping in finding their best condition with a smaller number of systematic experiments; thus, saving time and expenses.

The main goal of this work was to achieve homogeneous copolymer using the optimization of the synthesis process. In this work, the response is how much the synthesized polymer is homogeneous. No need to say, experimenters commonly detected this property by his or her eyes. To avoid the error of eye detection, we propose the combination of experimental design method and image analysis to find the optimal condition of a copolymer synthesis. Given that the advantages of vinyl acetate-butyl acrylate copolymer latex for seed coating, we selected this polymer as a target. Image analysis was used to quantify the homogeneity and the polymer was synthesized at optimal condition and then characterized by different methods. Subsequently the coating of this polymer on sugar beet seeds under low temperature was evaluated.

2. Experimental procedure

2.1 Materials and method

Butyl acrylate (BuA) and vinyl acetate (VAc) were purchased from Samchun Company. Both monomers BuAc and VAc were distilled under vacuum to remove the inhibitor. Potassium Persulfate (KPS), Sodium bicarbonate, Sodium lauryl sulfate (SLS), Azo-bis isobutronitrile (AIBN) and Ammonium Persulfate (APS) is supplied by Merck and consumed as received. The glass transition temperature of the polymers is determined by Differential Scanning Calorimeter (DSC) [Mettler Toledo]. The measurement is usually carried out from -100°C to 50°C at 10°C/min under N₂-atmosphere. The T_g is determined by the midpoint of the transition region. Polymerization reactions were monitored in-line using an Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) spectrometer (Golden Gate). Particle size was measured by Mavern Mastersizer 2000 ver. 5.1. The

instrument covered a size range from 0.02 to 2000 μm. The morphology of samples was observed from Scanning Electron Microscopy (SEM) images which were obtained using a (Leo 1455vp) scanning electron microscope.

To assess the properties of synthesized polymer for the coating of sugar beet seeds, seeds coated with temperature-sensitive polymer and conventional polymer and uncoated seeds were tested. The treated seeds were sown at 2 cm depth in Research Farm of Sugar Beet Seed Institute (SBSI) of Karaj, Iran on February 2, 2016. The between-row and on-row spacing were 50 cm and 5 cm, respectively, and the row lengths was 5 m. The study was carried out as a randomized complete block design in four replications, each one composed of 100 seeds for each individual treatment. Effective precipitation obviated the need for irrigation.

2.2 Polymerization condition

Polymerizations were carried out with constant stirring in a 3-neck round-bottom glass flask equipped with a sampling port, reflux condenser, and thermometer. The system of copolymerization temperature was held constant by an oil bath. First the deionized water, buffer (NaHCO₃) and anionic surfactant (SLS) were stirred. Ten minutes later, one third of the whole monomers and initiator were mixed and after which the residual monomers mixture was slowly added to the flask. The gradual addition of monomers makes in a high quality copolymer. The emulsion polymerization experimental conditions are summarized in Table 2.

3. Results and discussion

3.1 Experimental design and achieving optimal condition of the parameters

There is a large amount of experimental designs in the literature to search the optimal level of the factors [28-30]. A full factorial design is defined by all possible combinations of the factors and their settings. When there are k factors for investigation and that each factor is set to m different levels. The number of possible factor combinations and their levels will then be m^k.

When the number of experimental variables increases, the number of experimental runs in a factorial design will rapidly become large and inconvenient. For a set of k variables, it is possible to make a selection of a smaller subset of the experiments in the full factorial design so that it is possible to estimate the desired effect. It is easy to select subsets that are $1/2$, $1/4$, $1/8$, $1/2^r$ of the full factorial design, that is a subset with $2^r \times 2^k = 2^{k-r}$ experimental runs. This nomenclature should be read as a 2^r fraction of a two-level factorial design with k variables.

Here, for copolymer synthesis, a 2^{6-3} fractional factorial design was chosen. This fractional factorial design requires only the preparation of eight experimental conditions. The factors and their levels

are listed in Table 1. The levels of factors were chosen based on some preliminary experiments.

Table 1. Factors and levels employed to build the 2^{6-3} fractional factorial design

Factors	Level	
	-	+
(VAc)%	43	57
(BuA)%	43	57
SLS ^a (g)	0.0079	0.0121
Initiator (KPS) ^b (g)	0.0079	0.0121
Time (h)	3.16	4.84
Temperature (°C)	65	68

^a Sodium lauryl sulfate

^b Potassium persulfate

The experiments were carried out according to a specific combination of the levels of all factors, as listed in Table 2.

Table 2. Design matrix and experimental data of the 2^{6-3} fractional factorial design

Exp. No.	VAc%	BuA%	Surfactant (SLS) ^a (g)	Initiator (KPS) ^b (g)	Time(h)	Temperature(°C)
1	57	43	0.0121	0.0079	3.16	68
2	57	43	0.0079	0.0121	4.84	65
3	43	57	0.0121	0.0121	4.84	68
4	43	57	0.0121	0.0079	4.84	65
5	43	57	0.0079	0.0079	3.16	65
6	43	57	0.0079	0.0121	3.16	68
7	57	43	0.0079	0.0079	4.84	68
8	57	43	0.0121	0.0121	3.16	65

^a Sodium lauryl sulfate

^b Potassium persulfate

At each condition, the polymer was synthesized; then all of the samples were photographed at the same place (the same ambient light) and with the same distance to the camera. As it is discussed in the following section, color measurements will be obtained from digitized images is a simple and cost-effective way to evaluate the homogeneity of the copolymer.

3.2 Image analysis

To make the different color images comparable, they were resized to 128×128 pixels as illustrated in Fig. 1. Next, the images were presented in grayscale intensities using the Matlab software. Afterwards, the histogram of gray images was obtained as shown in Fig. 2, where zero and 250 values in x-axis codes the black and white colors, respectively. The y is the frequency of each color in the gray-scale.

It should be noted that, for some samples, the heterogeneity can be identified easily by our eyes, e.g, samples 4 and 7 as their related histograms show two maxima; it means the presence of two phases. However, we cannot decide which one is the most homogeneous sample among 8 samples because the others showed similar appearance. It can be seen in Fig. 2, x8 panel the sample 8 shows only one maxima and the shape of the histogram is more similar to the normal distribution which is a verification of one component, *i.e.*, homogeneous solvent. Thanks to the advantage of this image analysis, we selected, the condition of number 8 as the optimal condition for the synthesis of the copolymer.

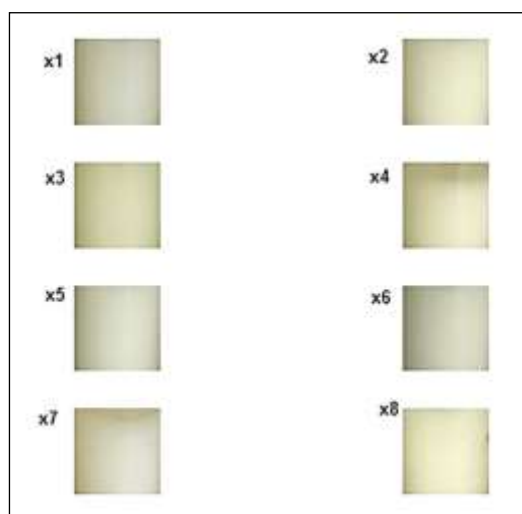


Fig. 1. The obtained images of sample 1 to 8 (x1 to x8) with 128×128 pixels

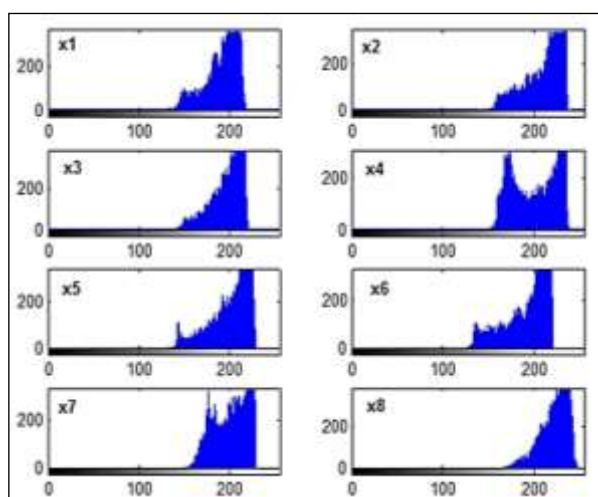


Fig. 2. histogram of the gray-scale images corresponding to figure 2; 0 and 250 codes black and white colors in x-axis . Y axis is counted.

3.3 Synthesis and characterization of vinyl acetate-butyl acrylate copolymer latex

After successful selection of the most homogenous copolymer using image analysis, the optimum condition (Table 2, entry 8) was used for synthesis of copolymer VAc/BuA with three kinds of initiators. The best reaction condition for maximum conversion was attained when the weight ratio of VAc/ BuA was 57%/43% in reaction time of 3.16h, reaction

temperature of 65°C, initiator concentrations and anionic surfactant of 0.0121 wt%.

Firstly, solid content and the conversion of copolymers were calculated by equations (1-1) and (1-2) [15, 27]:

$$\text{Solid content (\%)} = \frac{\text{Dry film weight (g)}}{\text{Wet film weight (g)}} \quad (1-1)$$

$$\frac{W_1 \times S + W_2 - W_3 - W_4}{W_0} \times 100\% \quad (1-2)$$

There is the relationship between these parameters and the Tg [17, 31].

When, W_1 = the whole output of latex, W_2 = the amount of latex, W_3 = the amount of initiator, W_4 = the amount of emulsifier, W_0 = the amount of whole monomers and S is the solid content of latex.

In this study, they were 32.2% and 87%, respectively. There is a difference between measured Tg and theoretical value of Tg. This difference may be due to conversion is 87%.

Fig. 3 (a)–(c) shows the ATR-FTIR spectrum of VAc/BuA copolymer, with different initiators (a) potassium persulfate (KPS), (b) ammonium persulfate (APS) and (c) azobisisobutyronitrile (AIBN), respectively. The C=O stretching absorption in 1728 cm^{-1} , the C–O stretching band in 1230 cm^{-1} and the C–H stretching absorption at 2956 cm^{-1} obviously confirmed that copolymerization has taken place between vinyl acetate and butyl acrylate [7, 32,33].

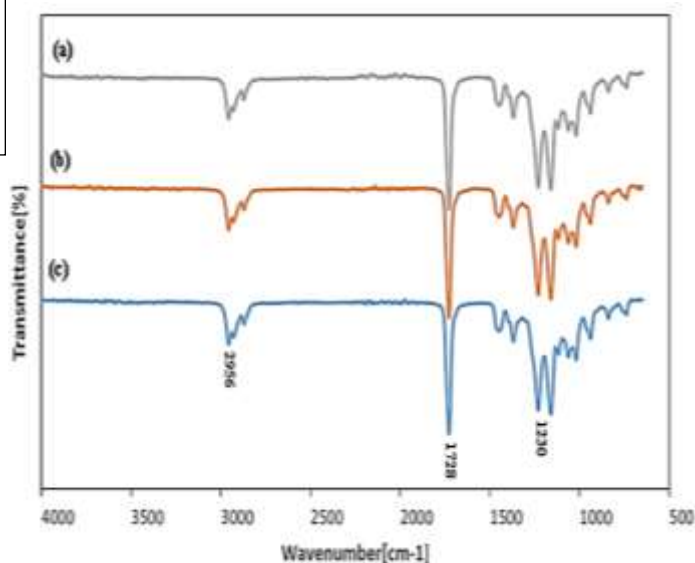


Fig. 3. ATR-FTIR spectra of optimized copolymer (VAc/BuA). With different initiators (a) KPS, (b) APS, (C) AIBN.

The differential scanning calorimetry curves of VAc/BuA copolymer in optimum condition, with different initiators were investigated and the result is depicted in Fig. 4. As it can be seen in Fig. 4, the T_g value in different initiators are similar [3, 27]. In addition, all the copolymers showed almost the same T_g value, indicating that these copolymers were mostly in very short blocks and homogeneous [34,35].

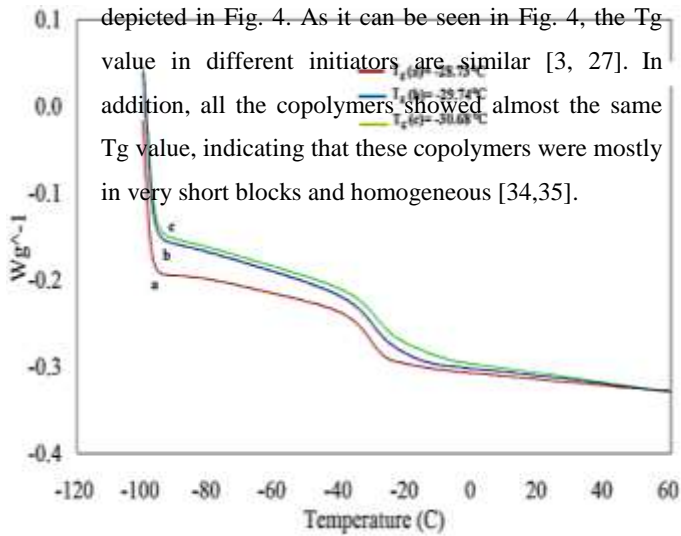


Fig. 4. DSC curves of optimized copolymer (VAc/BuA) with different initiators (a) KPS, (b) AIBN, (C) APS

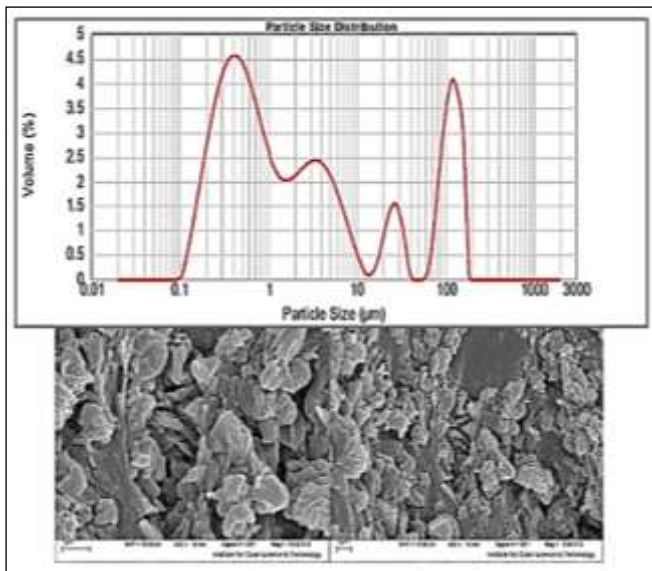


Fig. 5. Particle Size Distribution (PSD) and SEM image of copolymer (VAc/BuA) with KPS as initiator.

Fig. 5 shows the particle size distribution (PSD) and SEM micrographs of the synthesized copolymer with potassium persulfate as initiator. The images showed the long-chain and elastic form of copolymer [25]. The

average PSD of latex shown moderate distribution of particle size (0.1- 100 µm)[6].

After synthesis and characterization of copolymer structure, its performance investigated for coating of sugar beet seeds, as explained in the experimental section (Fig. 6).



Fig. 6. The coated sugar beet seeds with synthesized copolymer (with KPS as initiator).

No germination was observed in the field for 32 days, but the germination commenced with temperature rise so that 27% uncoated seeds, 18% seeds coated with the conventional polymer (it was used poly-vinyl acetate), and 10 seeds coated with the delayed copolymers germinated by March 11, 2016. All treatments were recorded again until April 27, 2016. The observations on March 31 and April 6 (Fig. 7) showed that 19 and 38 seeds coated with the delayed copolymer had germinated whereas the germination was observed in 33 and 74 uncoated seeds and 32 and 74 seeds coated with the conventional polymer, respectively. It implied that the newly synthesized copolymer could refrain the seeds from germination for about one month and afterward, the coated seeds germinated like all other treatments so that the number of the germinated uncoated seeds, germinated seeds coated with the conventional polymer and those coated with the synthesized polymer was 90, 103 and 105 in April-16 reading, respectively [24-25].

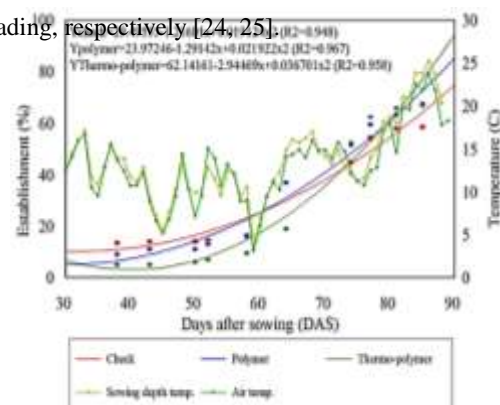


Fig. 7. The seeds from germination for about one month. The results show that after the suitable conditions were provided for the germination (about 40 days), the synthesized copolymer was able to control germination.

4. Conclusion

The experimental design and image analysis showed that the optimum conditions to synthesize a copolymer was the reaction of vinyl acetate/butyl acrylate in the presence of different initiators at 65°C within 3.16 hour. This copolymer was found to effective for sugar beet seed coating. The coated seed displayed enhanced performance against disease and undesirable weather condition. Also, applying a polymer coating to the seeds of other crops could be economically beneficial for autumn sowing. However it is imperative to do further work on enhancing the efficiency of the temperature-sensitive synthesized polymer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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