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Effect of latex conversion on glass transition temperature

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ABSTRACT

We have synthesized styrene-acrylic latex and investigated the effect of such reaction conditions as the dosage of initiator, surfactant and stirring speed on monomer conversion and glass transition temperature (Tg) of polymer by means of orthogonal experiment, then we get the best reaction conditions. Test results prove that the glass transition temperature of the polymer is directly related to the monomer conversion. The improvement of monomer conversion can make the glass transition temperature close to the theoretical value. In the case of high final conversion, we can predict the glass transition temperature of the polymers of different composition according to the theoretical relation effectively.

Keywords: Monomer Conversion; Orthogonal Experiment; Glass Transition Temperature

1. INTRODUCTION

Styrene-acrylic latex is made of styrene and acrylate monomers, which has many advantages. For example, it has wide source of raw materials, high function/price ratio, simple synthetic process and the latex has outstanding water resistance, alkali resistance, scrub resistance and also the paint film has good outdoor durable, adhesive attraction. So the styrene-acrylic latex has been widely used in building coating, metal surface coating and so on. Many researchers [1-5] have studied styrene-acrylic latex. Climates are usually diverse across countries, even in one country. Therefore, a single recipe cannot satisfy different needs in the different climate. In order to adapt to different environment, especially the temperature environment, it requires the minimum film-forming temperature can not only has an unchangeable temperature. Scholars in this area had focused mostly on performance optimization but ignored the investigation of minimum film-forming temperature. In fact, there is a big difference between actual minimum film-forming temperature and theoretical minimum film-forming temperature, which brings polymer designers difficulties in predicting glass transition temperature and designing the hardness of the polymer, at the same time, brings users a lot of inconvenience in use. There are many reasons for the difference between actual minimum film-forming temperature and theoretical minimum film-forming temperature, one of the most important is the monomer conversion. Due to the minimum film-forming temperature has a good corresponding relation with the glass-transition temperature [6], so this paper mainly investigates the glass-transition temperature by means of optimizing the latex's polymerization conditions. We obtain latex with high conversion, thus we can solve the above problems in polymerization technology aspect and obtain the latex recipe of different glass transition temperature under the guidance of the theoretical relation.

2. EXPERIMENTAL

2.1. Materials

Butyl acrylate (BA, 96%), Styrene (St, 97%), Methyl Methacrylate (MAA, 96%) and Diacetone acryl amide (DAAM) were purchased from Qingdao Reagent Company. The anionic surfactant sodium dodecyl sulfate (SDS), nonionic surfactant nonylphenol polyoxyethylene ether (OP-10) and ammonium persulfate (APS) were purchased from Qingdao Chemistry Reagent Company. All materials were used without further purification.

2.2. Preparation of Styrene-Acrylic Latex

All emulsifier and deionized water were feeded into four-necked flask and stirred at high speed first, then feed monomer mixtures slowly to obtain the beforehand latex. Take part of beforehand latex for seed latex, when temperature was wormed up to 75 ± 1℃, feed

part of initiator solution. After the blue seed latex formed, the remaining latex was fed gradually, and partially drop initiator, beforehand latex and initiator were added respectively in 3.5 h and 4 h. Then the temperature was heated to 85 ± 1℃ and kept this temperature for 1 h, then cooled, adjusted PH = 7-8, Filtered and Collected latex at last.

2.3. Characterization

The test of solid content:

$$s = \frac{m_1}{m_0} \times 100\%$$

where s is the solid content of latex, m_1 is the weight of the latex after dried at 80℃ in vacuum drying oven, m_0 is the weight of the latex.

The test of monomer conversion:

We calculate the conversion by below relation

$$C(\%) = \frac{W_1 \times S + W_2 - W_3 - W_4}{W_0} \times 100\%$$

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

The theoretical value of copolymer's glass transition temperature:

Using the following FOX relation, we can get the composition of copolymers which have an expectable Tg.

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} + \frac{W_3}{Tg_3} + \ldots\ldots \frac{W_n}{Tg_n}$$

where Tg is the glass transition temperature of copolymers, Tg_1, Tg_2, Tg_3, Tg_n are the glass transition temperature of the respective homopolymers and W_1, W_2, W_3, W_n are the weight fraction of the respective groups.

2.4. Differential Scanning Calorimeter (DSC) Analysis

Tg was measured by the DSC method in a NEYZSCH 204F1 type differential scanning calorimeter for polymer samples of ~20 mg. DSC condition measurement: hold for 1.0 min at –100℃, heat from –80 to 100℃ at 10℃ min^{-1} and with nitrogen protection.

3. RESULTS AND DISCUSSION

3.1. Choice of Variables and Level of the Orthogonal Experiment and its Results

During the experiment we found that there is a big difference between measured value and theoretical value of Tg (the theoretical value is calculated by FOX relation). After analysis, the author believes that the main reason of this phenomenon is due to a lower conversion of polymerization, the system was not polymerized according to the expectable proportion, so we do the experiment to optimize the process parameters of polymerization by orthogonal experimental firstly in order to obtain the latex with high monomer conversion.

Based on a large number of references and many repeated experiments, we consider that the dosage of initiator (A), Emulsifier (B) and stirring speed (C) are the main factors of polymerization, and have designed L9 (3^3) orthogonal table (three variables, three levels Orthogonal design), the results are shown in **Table 1**.

3.2. The Analysis of Orthogonal Experiment Results

The weighted average (K) and range (R) are given in **Table 2**.

Table 2 shows that the sequence of the effect of various factors on conversion is emulsifier > initiator > stirring speed, the best condition is $A_3B_2C_2$: initiator: 0.8%, emulsifier: 4%, stirring speed: 180 rpm. But we can see that the difference between k_2 (88.033) and k_3 (89.000) is very small, and as we know the conversion increase with the increase of the initiator, but the gel will increase obviously and the polymerization will become unstable at the same time, so we choose $A_2B_2C_2$: initiator: 0.6%, emulsifier: 4%, stirring speed: 180 rpm at last.

Table 1. Test results.

Test NO	A %	B %	C rpm	Conversion %
1	1(0.4)	1(2)	1(140)	82.6
2	1	2(4)	2(180)	90.0
3	1	3(6)	3(240)	78.3
4	2(0.6)	1	2	87.6
5	2	2	3	92.5
6	2	3	1	84.0
7	3(0.8)	1	3	90.0
8	3	2	1	91.0
9	3	3	2	86.0

Table 2. The analysis of experiment results.

Test Indicators		A	B	C
conversion	k_1	83.633	86.733	85.867
	k_2	88.033	91.167	87.867
	k_3	89.000	82.767	86.933
	R	5.367	8.400	2.000

Table 3. Properties of the latex under the condition of $A_2B_2C_2$.

solid content (%)	gel (%)	water absorption(%)	Conversion(%)
48.6	3.5	7	94

As shown in **Tables 1** and **2**, the final conversion can reach 94% under the condition of $A_2B_2C_2$ and it is higher than the others, in addition, some other properties are ideal too.

3.3. DSC Test Analysis

In this paper, the initial composition of monomer is BA: MMA:St = 33:19:18, the theoretical value of Tg which is calculated by FOX relation is 8℃. But when we adopt the flowing factor: initiator: 0.6%, emulsifier: 4%, speed: 180 rpm, the final conversion reaches 94% and the measured value of Tg achieved by DSC test is 9.8℃ (**Figure 1**), the difference between them is small. That is to say at the condition of high conversion, the measured value of Tg is very close to its theoretical value and so we can design the hardness of copolymers according FOX relation.

3.4. The Relationship of Monomer Conversion and Glass Transition Temperature

Figure 2 shows us the relation between Tg and monomer conversion (BA:MMA:St = 33:19:18) and we can see from it that with the increase of the monomer conversion, the glass transition temperature of the latex decrease gradually, when the final conversion is over 90%, Tg reaches a plateau and the value is about 10.0℃. The mainly reason is that during the radical copolymerization, when the final conversion is low, the monomer with a strong conjugacy is easier to polymerize than the others, styrene is such a hard monomer and the glass transition temperature of its homopolymer is 105℃, so the Tg of copolymer will be a little higher than usual; on the contrary, when the final conversion is high, the system is able to polymerize according to the expectable proportion, the measured value and theoretical value of Tg match very well. However, the conversion of polymerization can not reach 100%. In addition, Tg will increase because of the hydrogen bonds formed between the Components [7]. Some references [8-11] introduce that some additives and functional monomers will have a certain impact on glass transition temperature, therefore, there will be a difference between measured and expected value of Tg inevitably.

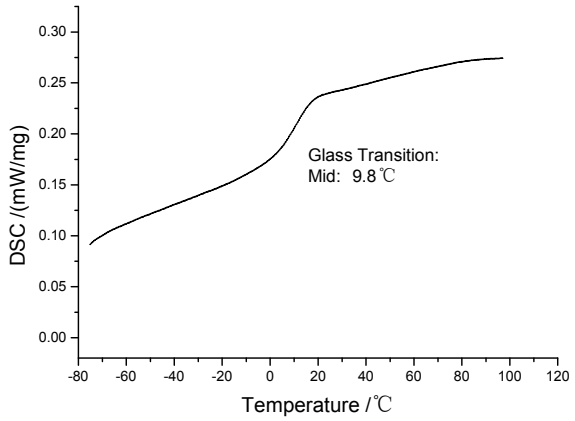

Figure 1. DSC curve of Styrene-acrylic latex (BA:MMA:St = 33:19:18).

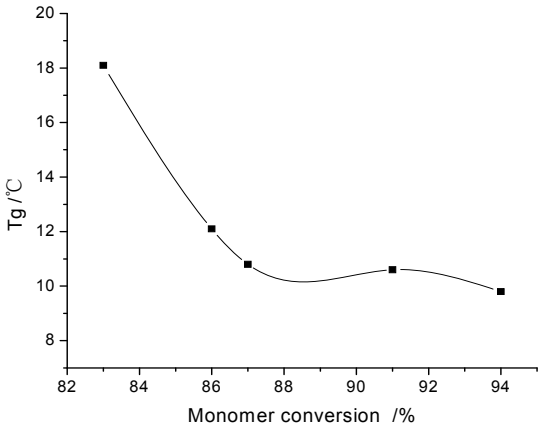

Figure 2. The relation between Tg and monomer conversion.

3.5. The Latex Recipe of Different Tg

In this paper, the total mass of the monomer is fixed at 70 g and the ratio of two hard monomer (St and MMA) will not change at about 1:1, we changes the proportion of soft and hard monomer only. **Table 4** shows the latex recipe with different Tg which are obtained at the condition of $A_2B_2C_2$.

Table 4 shows that when the final conversion is at a high level, the measured value and theoretical value of Tg matches very well, thus researcher can be able to forecast the Tg of polymer according to the proportion monomers.

4. CONCLUSIONS

1) The results of the orthogonal experimental shows that emulsifier > initiator > stirring speed in terms of their effects on conversion. And we get the best condition: emulsifier 4%, initiator 0.6%, stirring speed 180 rpm.

Table 4. Latex recipe with different Tg.

	BA(g)	MMA(g)	St(g)	theoretical value of Tg	measured value of Tg
1#	48	11	11	–20.0℃	–18.3℃
2#	43	14	13	–10.0℃	–9.3℃
3#	38	16	16	–3.0℃	–2.2℃
4#	33	19	18	7.8℃	9.8℃
5#	28	21	21	20.0℃	20.4℃
6#	26	22	22	24.0℃	25.2℃
7#	24	23	23	30.0℃	32.7℃
8#	20	25	25	40.0℃	42.7℃
9#	17	27	26	45.0℃	46.9℃

2) There is a direct relationship between conversion and glass transition temperature, the improvement of the final conversion has made the measured value close to the theoretical value.

3) At the condition of high conversion, the measured value and theoretical value of Tg matches very well.

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