The kinetics study and reaction mechanism of acrylate grouting materials

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Acrylate grouting material has been widely used in dams, tunnels and other underground buildings. This paper introduces the basic components of acrylate grouting material, then the reaction mechanism and dynamics of gelation process are discussed based on the theory of free radical polymerization. By measuring the relationship between gelation time and the concentration of initiator ammonium persulfate, the chain termination of free radical is confirmed to be single-base termination reaction. The gelation time is inversely proportional with the concentration of initiator and is directly proportional to the natural logarithm of the ratio of the initial concentration $[M]_0$ and a time component concentration $[M]$ of the acrylate monomer. The quantitative relation between them was derived. The result has a guiding significance on the material design and the gelation control of acrylate grouting material.

Key words: Kinetics, Reaction mechanism, Grouting material, Acrylate.

INTRODUCTION

Chemical grouting is a common method for the treatment of waterproof sealing [1, 2]. Chemical grouting material was filling into the formation or crack, which diffused, coagulated and cured, to increase the formation strength, reduce the permeability of the formation[3], prevent the formation of deformation[4, 5], or repair of cracks on concrete building[6, 7]. Acrylate is an important kind of chemical grouting material. Since the United States halted sales of acrylamide grouting in 1978 because of the pollution risk, the research and application of acrylic acid salts grouting material got the attention of the countries [8]. In 1980, acrylate polymer (AC-400) slurry began to instead of acrylamide grout materials. The AC-400 used now is the mixture of calcium, magnesium acrylate monomer, a small amount of methyl double acrylamide, triethanolamine, ammonium persulfate and water. In the 70s, China began to study acrylate grouting materials. The Changjiang River Scientific Research Institute carried out a study of acrylamide non-toxic alternatives, develop less toxic acrylic mixed salts of calcium and magnesium, which was successfully applied in Wan'an hydropower and dam seepage in the Three Gorges Project.

In recent years, a new crosslinking agent instead of methylene-bis-acrylamide was developed making acrylate grouting material more accord with the requirement of environmental protection, at the same time there is the component increasing inflation performance as well as antagonists to eliminate the toxicity, and it improved the production technology to make them more outstanding performance [9]. To synthesize a kind of environmental crosslinking agents, and a water-soluble, non-toxic, replacing the original acrylic chemical grouting material used methylene bis-acrylamide cross-linker solved methylene bis-acrylamide difficult to dissolve and pollute the environment. This kind of crosslinking agent as raw materials in the preparation of acrylate chemical grouting material has low viscosity, good fluidity, can be poured into the tiny cracks in the gelation time control, low permeability, and high compressive strength of solid sand. Acrylate grouting material has been used in the dam foundation tunnels, sewers, underground buildings plugging and weak strata stabilization process, as well as other aspects of drilling wall has been widely used. Han's group explored the dynamics of gelation time in the oxidant ammonium persulfate and reductant sodium thiosulfate.

The reaction mechanism of grouting material is important because they can direct the actual application in engineering [10]. The kinetics of acrylate in ammonium persulfate oxidizer and triethanolamine accelerator was rarely reported. In this paper, bases on the theoretical basis of the radical polymerization, the reaction mechanism of acrylate grouting material in the present of the oxidizer ammonium persulfate and triethanolamine

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accelerator were described and the reaction kinetics of acrylate grouting material was discussed.

EXPERIMENTAL

The basic compositions of the chemical grouting material are the acrylate, crosslinking agent, initiator, accelerator, retarder and water. The crosslinking agent has two or more functional group which can be reacted with the primary agent. The gelation time can be controlled by adjusting the amount of retarder in the slurry between several minutes to several tens of minutes. There are a lot of acrylate monomer can be used in grouting, such as calcium acrylate, magnesium acrylate, zinc acrylate, potassium acrylate and sodium acrylate. Calcium acrylate was added as antagonists to get a lower toxicity and good performance of the gel. In this paper the mixture of calcium acrylate and magnesium acrylate solution were selected as the main agent.

Through a large number of tests, the best proportion of basic composition was determined, shown in Table 1.

Table 1. The basic composition of acrylate grouting material.

Materials composition	Mass percentage (%)
Acrylate monomer	10～20
Accelerant	1～2
Crosslinker	2～5
Initiator	0.5～2
Solvent	70～80
Retarder	be adjusted according to the curing time

RESULTS AND DISCUSSION

Radical polymerization mechanism

Acrylate grouting material is carried out in accordance with the mechanism of free radical polymerization. Radical chain polymerization is a chain reaction, consisting of a sequence of three steps: initiation, propagation, and termination.

With ammonium persulfate as initiator and triethanolamine as accelerator in water, primary free radicals formed and stimulated the acrylate monomers coupled to double bond structure of crosslinking agent. The primary radicals inspired by acrylate monomer could form monomer free radicals. Polymer with space network was formed structure by radical polymerization. Retarder can capture the primary radicals and extend the time of the combination of free radicals and monomers,

which made the induction period of polymerization longer, thereby controlling the gelation time.

It is assumed that the initiator ammonium persulfate generate the primary radical. (M, acrylate monomer or crosslinking agent; Mn•, the growing polymer chain) According to the theory of free radical polymerization, each elementary reaction expression was discussed as follows:

Step 1: Chain initiation

Chain initiation is the reaction of forming free radical of monomer, consisting of the following two steps. The first step is that the initiator decomposed to form a primary radical R •.

$$I \xrightarrow{k_d} 2R \cdot \text{, (1)}$$
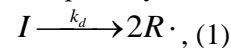
where k_d is the rate constant for the initiator dissociation

The second step is that monomer free radicals formed with the addition of monomer to primary radicals

$$\text{, (2) } R \cdot + M \xrightarrow{k_i} RM \cdot$$
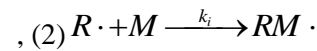
Step 2: Chain propagation

As the propagation continues, each monomer unit was added. The radical has the same identity as the previous radical. Therefore, Eq.(3) of chain propagation was shown as following:

$$RM \cdot + M \xrightarrow{k_p} RMM \cdot \xrightarrow{nM} RMMnM \cdot \longrightarrow$$
$$\longrightarrow \cdots\cdots \longrightarrow RMn \cdot \text{, (3)}$$
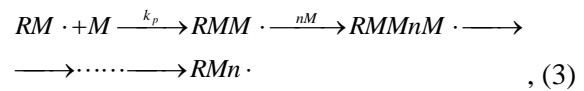
In which k_p is the rate constant for the Chain propagation.
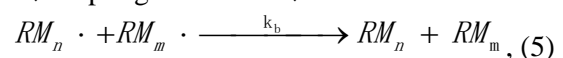
Step 3: Chain termination

The growth of the chain takes place very rapidly to form higher weight polymer. But at some point, the polymer chain stops growing because the propagating radical could be terminated at the end.

The termination of the radical occurs by the bimolecular reaction between two radicals. They reacted with each other by coupling or disproportionation.

The two different modes of termination can be expressed as following:

$$RM_n \cdot + RM_m \cdot \xrightarrow{k_a} RM_{(n+m)}R \text{, (4)}$$
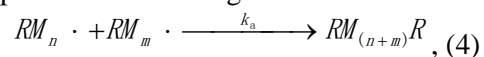
（Coupling termination）

$$RM_n \cdot + RM_m \cdot \xrightarrow{k_b} RM_n + RM_m \text{, (5)}$$

(Disproportionation termination）

In which k_a and k_b are the rate constants for terminations by coupling and, respectively.

Free radical polymerization kinetics of acrylate grouting material

The polymerization process of acrylate grouting material includes chain initiation, chain propagation and chain termination. Here the reaction rate of the reaction material (monomer and crosslinking agent) is represented. According to the law of mass action, the reaction rate equation can be derived.

The chain initiation rate equation was shown as following:

$$R_d = d[R\cdot]/dt = 2fk_d[I] \tag{6}$$

In which k_d denotes the rate constant of chain initiation, R_d denotes the reaction rate of chain initiation, f denotes the initiator efficiency of initiation, and $[I]$ denotes the concentration of the initiator.

The overall rate of polymerization (R_p) can be considered as the rate of disappearance of monomer with respecting to time of $d[M]/dt$. This depletion is due to the initiator-monomer reaction and the propagation reaction.

$$R_p = -d[M]/dt = k_p[M\cdot][M] \tag{7}$$

In which k_p denotes the rate constant of the chain propagation, $[M]$ denotes the concentration of monomer and crosslinker, $[M\cdot]$ denotes the total concentration of all the radical.

The rate of chain termination (R_t) can be considered as the disappearance rate of all the monomer radical, with respecting to time $d[M]/dt$, including coupling and disproportionation termination:

$$R_t = -d[M\cdot]/dt = 2k_t[M\cdot]^2 \tag{8}$$

In which k_t denotes the rate constants for termination by coupling and disproportionation, and k_t is the sum of k_a and k_b.

In theory, three basic assumptions were introduced in polymerization kinetics, as the activity, large degree of polymerization and steady process. With three basic assumptions, the basic equations of polymerization kinetics can be introduced as following.

$$R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^a \tag{9}$$

In which a is a reaction coefficient between 0.5 and 1.

In Eq.(9) R_p is also the consumption rate of monomer M, so R_p may be expressed as:

$$R_p = -d[M]/dt \tag{10}$$

Supposing the starting concentration of monomer M equals $[M]_0$, the combining of Eq.(9) and Eq.(10) can yield the time t as

$$t = \frac{I_n \dfrac{[M]_0}{[M]}}{k\left(\dfrac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}} = \frac{I_n \dfrac{[M]_0}{[M]}}{k[I]^{1/2}} \tag{11}$$

Eq.(11) shows the relation between gelation time t and monomer concentration $[M]$, with reaction rate constant of k.

According to kinetics theory, free radicals reacted with one another to be terminated by coupling, and the rate of polymerization is proportional to the square of initiator concentration. When they react with one another to be terminated by disproportionation, the rate of polymerization is proportional to the initiator concentration. One molecule of acrylate could form free radicals. Therefore it is impossible for one molecule of acrylate to be terminated by coupling. So Eq.(11) is transformed into Eq.(12).

$$t = \frac{In \frac{[M]_0}{[M]}}{k_p \left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}} \tag{12}$$

Eq..(12) shows that the gelation time is inversely proportional to ammonium concentration of persulfate initiator in temperature constant

For a given concentration of acrylate materials, the ratio $[M]_0/[M]$ is fixed at different process of solidification. When the grouting material gels, Eq.(12) is transformed into the Eq.(13):

$$C = t \times [I] \tag{13}$$

To verify the correctness of the above Eq.(12), a set of experimental data was done (in Table 2), showing the influence of ammonium persulfate dosage on the gelation time.

If equation (12) is correct, the gelation time t multiplied by the concentration of ammonium persulfate should be a constant. So the data in Table 1 was plugged into equation (13) to calculate the value of product concentration C, when the concentration of ammonium persulfate was different (Table 3).

In Table 3, C is basically a constant. The results show that the gelation time of acrylate grouting material is inversely proportional to concentration of catalyst ammonium peroxydisulfate. Eq.(12) shows the relation between gelation time and initiator concentration. It also could been obtained that the acrylate grouting material chain termination reaction is a single-terminated reaction.

Table 2. Effect of $(NH_4)_2S_2O_8$ on the gelation time.

Concentration $(mol \cdot L^{-1})$	0.0286	0.0491	0.07365	0.0982
Gelation time (s)	163	95	63	47

Note: Concentration of acrylate grouting material equals 25%, concentration of triethanolamine equals 1.0%, and the temperature is 25°C.

Table 3. The relationship of ammonium peroxydisulfate concentration and product concentration.

Concentration $(mol \cdot L^{-1})$	0.0286	0.0491	0.0736	0.0982
Product concentration C	4.66	4.66	4.64	4.62

CONCLUSIONS

The reaction mechanism acrylate grouting material belongs radical polymerization reaction. The gelation time is inversely proportional with the concentration of initiator ammonium persulfate and is directly proportional to the natural logarithm of the ratio of the initial concentration $[M]_0$ and a time component concentration $[M]$ of the acrylate monomer. The quantitative relation between them is given. Its mathematical formula can be concluded. This formula has a guiding significance on gelation time for the formula design and the construction control of acrylate grouting material.

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