Effect of additives on the mechanical properties of bulk polymerized Acrylic using orthogonal test

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Abstract. The effects of different additives on mechanical properties of acrylic were studied by orthogonal test, using methyl methacrylate as raw material, concentration of initiator (azobisisobutyronitrile), plasticizer (Dibutyl Phthalate) and release agent (Stearic Acid) as the influence factors. The results show that: among the three additives, initiator is the most significant factor, which has the greatest impact on the mechanical properties of acrylic. With increasing of initiator content, the tensile strength of acrylic decreases. The effect of plasticizer and release agent on the mechanical properties of acrylic is relatively small. As the increase of plasticizer content, the tensile strength and bending strength decline. Finally, the best ratio of the three additives is initiator=0.06, plasticizer=3.0, release agent=1.0.

1. Introduction

Acrylic (Poly methyl methacrylate, PMMA) is being widely used in Bearing Pressure Equipment thanks to its good comprehensive mechanical properties[1], such as building structure, aerospace, medical equipment, physical research. For the underwater manned vehicles, such as pressure hulls and submersibles, the primary focus of acrylic application is on the construction of observation windows on opaque pressure structures[2]. But there are still many blind spots for the crew unless the whole spherical shell is made of acrylic. The research on panoramic windows was ongoing until the U.S. Navy launched a spherical acrylic submersible named NEMO (DSV 5) in 1970[3], marking the beginning of the ultimate in underwater visibility[4].

The conventional manufacturing methods of pressure vessels are thermoforming and bulk polymerization casting, and the thickness of bulk polymerization casting is more uniform. In the process of bulk polymerization, the amount of initiator, plasticizer, release agent and other factors will affect the final performance of PMMA.

Extensive researcher concerning the influence of these factors on the performance of PMMA. For instance, S. T. Balke[5] reported an experimental investigation of the chemical-initiated bulk polymerization of methyl methacrylate(MMA) at different temperatures, and measured the change in the cumulative differential molecular weight distribution (CDMWD) with respect to conversion. Ida Poljanšek[6] observed that the molecular weight decreased with the increase of initiator concentration,
and decreased with the increase of conversion at high concentration. Chiemi Hirabayashi[7] found that compared with benzoyl peroxide (BPO) and other conventional initiators the residual MMA with tributylborane (TBB) as initiator in polymerization of PMMA decreased more rapidly, sustained for a longer time, and high molecular weight PMMA was first formed, then gradually decreased with time. In addition, the Ma. S.’s study[8] also confirmed that PMMA have a narrower molecular weight distribution by using ultrasound irradiation as initiator in polymers fabricated. Besides, temperature[9], time[10], pressure[11] and loading conditions[12] also have great influence on it.

Although there are lots of published studies on the preparation and properties of the PMMA, the current researches focus on the modification of single factor in the polymerization of the plexiglass composites, ignoring the interaction between different factors. In this paper, based on the bulk polymerization method of PMMA, initiators, plasticizers and release agents are selected as the research objects. By changing the ratio of various additives, the effects of additives on the properties of PMMA and the interaction between additives are studied. It is an important work to study the interaction between various factors and find out the best ratio of various factors. The main purpose of this paper is to confirm the interaction and dosage of additives, so as to lay a foundation for the overall pouring pressure structure.

2. Experimental

2.1 Materials

In this study, MMA (density of 0.944g/cm³, 99% purity) was produced by Jilin Petrochemical Company, which conforms to the national standard. Other additives like azobisisobutyronitrile (AIBN, recrystallization 99% purity) as initiator, dibutyl phthalate (DBP, 99% purity) as plasticizer and stearic acid (SA, 95% purity) as mold release agent are all purchased from Aladdin Company.

2.2 Experimental design

In the study of multi factor and multi-level experiments, the orthogonal test method is generally used to screen the factor level. The additives used in this experiment were AIBN, DBP and SA. L_{9}(3^{4}) orthogonal design table was selected, as shown in Table 1.

| Factor | Level |
|--------|-------|
|        | 1     | 2     | 3     |
| AIBN/% | 0.1   | 0.15  | 0.06  |
| DBP/%  | 3.0   | 4.0   | 5.0   |
| SA/%   | 0.8   | 1.0   | 1.2   |

2.3 Experimental process

PMMA sheets were prepared by step polymerization.

1) Pre-polymerization: Mixed the initiator, plasticizer and release agent with MMA monomer according to different formulations. The polymerization was carried out at 90° for 13 minutes in thermostat water bath. When the reaction solution became sticky, took it out and cooled down to room temperature immediately.

2) Post-polymerization: Poured the cooled solution into the mold and placed the mold in a 50° incubator for 24h. Then raised the temperature to 100°, last for 1 hour.

3) The PMMA specimens were machined into dumbbell shape according to the standard and then tested by universal testing machine at room temperature.
3. Results and analysis

Table 2. Experimental parameters (%).

| Num. | AIBN | DBP | SA |
|------|------|-----|----|
| 1#   | 0.1  | 3.0 | 0.8|
| 2#   | 0.1  | 4.0 | 1.0|
| 3#   | 0.1  | 5.0 | 1.2|
| 4#   | 0.15 | 3.0 | 1.0|
| 5#   | 0.15 | 4.0 | 1.2|
| 6#   | 0.15 | 5.0 | 0.8|
| 7#   | 0.06 | 3.0 | 1.2|
| 8#   | 0.06 | 4.0 | 0.8|
| 9#   | 0.06 | 5.0 | 1.0|

As shown in Table 2, 9 groups of samples were prepared according to different proportions, and the mechanical properties of each group of samples were tested.

3.1. Results

Uniaxial tensile test and three-point bending test were carried out at room temperature with the quasi-static strain rate of 0.0015/s. Each group of tests are repeated for 5 times, and the stress-strain results are shown in Fig. 1 and Fig. 2.

Fig. 1 shows the tensile stress-strain curve, and Fig. 2 is the three-point bending stress-strain curve. It can be seen from the figure that PMMA occur brittle fracture at room temperature, without yield process, and the stress-strain curves are nonlinear. Each group of curves are basically coincident at the beginning(within 1% of the strain), and the difference becomes obvious when the strain reaches 1.5%. The slope of curves decreases, that is, the elastic modulus decreases.

Fig. (a) (b) (c) in Fig. 1 and Fig. 2 are the curves of single factor test of AIBN, DBP and SA respectively. It can be seen that the three curves in Fig. (a) are almost coincident, only the fracture position is different, while the curves in Fig. (b) and Fig. (c) are obviously stratified. The results show that the content of AIBN plays a decisive role in the rate of slope decrease of PMMA performance curve. DBP and SA only affect the fracture position of PMMA, that is, the tensile strain.

Fig. 1. Tensile stress-strain curves of PMMA.
Fig. 2. Three-point bending stress-strain curves of PMMA.

3.2 Intuitive analysis
The results for fracture stress analysis of the test are shown in Table 3, I, II, and III are the mean value of experimental data corresponding to the same level, and R is range value. It can be seen from Table 3 that AIBN is the leading factor, and its impact on PMMA is significantly greater than the other two factors.

Through the calculation of I, II, and III, it can be seen that as the level of each factor changing, the fluctuation of index is not affected by the level of the other factors. The relationship between factors and indexes is shown in Fig. 3, from which it can be concluded that the optimal scheme of uniaxial tensile test is A3, B2, C2, while A2, B1, C3 is the best selection for three-point bending tests. Moreover, the influence of AIBN on PMMA performance fluctuates more than the other two additives.

The bending stress can be regarded as a combination of compressive stress and tensile stress, and the compressive stress of PMMA is far greater than the tensile stress. Therefore, the optimal ratio should be selected to optimize the tensile properties of the scheme. Although A2 is the best performance item in the three-point bending test, it is the worst item in the tensile test. Comprehensive analysis showed that the optimal formula was A3, B1 and C2.

Table 3. Experimental parameters (%).

| Num. | AIBN | DBP | SA  | $\sigma_T$ | $\sigma_B$ |
|------|------|-----|-----|------------|------------|
| 1#   | 0.1  | 3.0 | 0.8 | 70.65      | 101.33     |
| 2#   | 0.1  | 4.0 | 1.0 | 75.08      | 97.43      |
| 3#   | 0.1  | 5.0 | 1.2 | 70.2       | 93.1       |
| 4#   | 0.15 | 3.0 | 1.0 | 71.61      | 109.12     |
| 5#   | 0.15 | 4.0 | 1.2 | 67.21      | 117.34     |
| 6#   | 0.15 | 5.0 | 0.8 | 64.78      | 110.99     |
| 7#   | 0.06 | 3.0 | 1.2 | 74.67      | 112.08     |
| 8#   | 0.06 | 4.0 | 0.8 | 74.48      | 102.96     |
| 9#   | 0.06 | 5.0 | 1.0 | 72.56      | 108.6      |
| I    | 71.977 | 72.310 | 69.970 |          |
| II   | 67.867 | 72.257 | 73.083 |          |
| III  | 73.903 | 69.180 | 70.693 |          |
| R    | 6.036  | 3.130  | 3.113  | $\sigma_T$ |

Primary factors: AIBN; DBP; SA
The analysis results illustrate that the optimal experimental scheme is not included in the nine groups of experiments that have been completed. This is because the nine tests arranged by orthogonal table are representative, which can comprehensively reflect the influence of each level of three factors on the mechanical properties, and the optimal scheme is the result of comprehensive analysis.

3.3 Variance analysis
The intuitive analysis is simple, intuitionistic and less calculation, but it cannot estimate the test error. To solve this problem, variance analysis can be carried out on the test results. The analysis of variance is summarized in Table 4. The correction number $C$ and total square sum $SST$ are showed as follows:

$$C = \frac{T^2}{n}$$  \hspace{1cm} (1)

$$SS_T = \sum \chi^2 - C$$ \hspace{1cm} (2)

where $n$ is the number of tests, $T$ is the sum of 9 experimental indexes. And the sum of squares of single factor have the following relationship:

$$SS_A = \frac{T_{\text{A}}^2}{k_a} - C$$ \hspace{1cm} (3)

where $T_{\text{A}}$ is the sum of experimental indexes at the same level of all factors, $k_a$ is the repetitions of factors at different levels.

Table 4. Analysis of variance.

| Source of variance | Sum of variable squares | DF | Average change | F value |
|--------------------|-------------------------|----|----------------|---------|
|                    | T                       | B  | T              | B       |         |
| AIBN               | 57.05                   | 364.35       | 2               | 28.53   | 182.18  | 9.43    | 4.27 |
| DBP                | 19.27                   | 16.14        | 2               | 9.64    | 8.07    | 3.18    | 0.19 |
| SA                 | 15.93                   | 11.86        | 2               | 7.97    | 5.93    | 2.63    | 0.14 |

$F_{0.1}(2,2)=9.0, F_{0.05}(2,2)=19.0, F_{0.01}(2,2)=99.0$
As can be seen in Table 4, the results of F-test show that the three factors have no significant effect on the performance. Since the influence is not obvious, there is no necessary to make multiple comparisons among the factors. In this case, the level combination with large average can be selected as the optimal combination from the table. That is to say, the conclusion of variance analysis is consistent with that of intuitive analysis.

Design-Expert 12.0 software is used to draw the 3D response surface of interaction effect of various factors, as shown in Fig. 4. It can be seen from the figure that the interaction between AIBN and the other two factors has a great influence on the maximum tensile strength and maximum bending strength of PMMA. With the increase of AIBN content, the tensile strength increases a little and then decreases rapidly, while the bending strength decreases first and then increases; DBP and SA have little influence on PMMA performance, and the interaction surface between them is almost a plane, as shown in Fig. 4(c) and Fig. 4(f), so their influence can be ignored.

3.4 Validation results
According to the results of intuitive analysis, the optimal combination of A3, B1, C2 was used to prepared PMMA under the same conditions, the test results are shown in Fig. 5. For the tensile test, the final test results are significantly better than the above 9 groups of tests; In the three-point bending test, the final test curve is between AIBN=0.15 and AIBN=0.06, which is consistent with the expectation. The experimental results verify the correctness of the orthogonal test method.
4. Conclusions
The uniaxial tensile and three-point bending responses of bulk polymerized PMMA specimens have been characterized over altering the ratio of additives in bulk polymerization via a series of uniaxial tensile and three-point bending tests. Based on orthogonal experimental theory, the major conclusions can be summarized as follows:

PMMA shows obvious brittle fracture and no yield limit under quasi-static load at room temperature; the additives AIBN, DBP and SA have certain effects on the properties of MMA bulk polymerization products. AIBN is the main factor, which has the greatest influence on the properties of PMMA: With the increase of AIBN content, the tensile strength of PMMA decreases, while the bending strength increases first and then decreases; AIBN mainly affects the decreasing speed of elastic modulus during tensile and bending tests, while DBP and SA affect the fracture strain (fracture toughness) of PMMA; The optimum ratio of PMMA prepared by bulk polymerization is AIBN=0.06, DBP=3.0, SA=1.0. The content of AIBN determines the initial elastic modulus of PMMA and the reduction rate of elastic modulus. When AIBN=0.06, the initial tensile elastic modulus of PMMA is the largest and the decreasing trend is the slowest. When AIBN=0.15, the initial three-point bending elastic modulus of PMMA is the largest and the decreasing trend is the slowest.

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