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Based on Orthogonal Experimental Analysis: Effects of Formulation Systems on the Mechanical, Heat Resistance, and Aesthetic Properties of High-Gloss Black PMMA/ASA Alloys

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Abstract

High gloss and heat resisting PMMA/ASA is applied in many fields such as automotive materials. There are many researches focusing on single properties but no comprehensive quantitative evaluation. In this work, we used orthogonal experiments and variance methods, along with a custom Python program, to conduct in-depth experimental analysis and provide a comprehensive evaluation of the performance of each component in the material system. The results demonstrate that this analysis method can appropriately assess the enhancements that each functional component contributes to corresponding performances. Additionally, it was observed that the strategy of blending high and low melt flow index PMMA affects the overall performance, as the application of high and low melt flow index PMMA changes the distribution and gradient of the functional components, significantly enhancing performance for certain surface or gradient-sensitive properties.

Keywords: *PMMA/ASA alloy; Orthogonal Experimental Analysis; classroom teaching*

1 Introduction

Poly (methyl methacrylate) (PMMA), is one of the most common non-crystalline, highly transparent engineering plastics. It is widely used in optical devices [1], consumer electronics[2-3], aerospace[4-5], automotive materials[6-7], and other fields[8]. In addition, the high transparency of PMMA allows it to achieve high gloss and high brightness effects, enabling aesthetic finishes such as high-gloss black and piano black [7, 9-10]. However, PMMA typically exhibits certain brittleness and insufficient heat resistance, often requiring the introduction of acrylonitrile-styrene-acrylate (ASA) copolymer to form PMMA/ASA alloys in order to improve its heat resistance and impact toughness[9, 11]. ASA resins offer better resistance to environmental stress cracking, improved processing performance, and excellent compatibility with PMMA and PC, making them widely used in modified plastic products[12- 13].

Current researches on PMMA/ASA alloys usually focuses on evaluating individual formulation components[7, 14-15]. Based on these studies, the general effects of different formulation systems on alloy properties can be assessed. However, there is still a lack of comprehensive and systematic evaluations of the reliability of these formulation systems. This paper will use orthogonal experiments and hypothesis testing methods to quantitatively evaluate the impact of various formulation systems on the performance and appearance of high-gloss black PMMA/ASA alloys.

2 Experimental

2.1 Materials

The materials used in this work are listed as below:

High melt index PMMA: CM 211, purchased from Chi Mei Corporation;

Low melt index PMMA: CM 205, purchased from Chi Mei Corporation;

Toughening agent: LP2068, purchased from Guangzhou Entropy Energy;

MABS: 758, purchased from Chi Mei Corporation;

MABS: 920, purchased from Toray Malaysia.

Antioxidants: 1076, 168, purchased from BASF.

2.2 Sample Preparation

According to the mixing-level orthogonal experiment, the materials were prepared based on the experimental formulation. After thorough mixing, the mixture was granulated using an twin screw extruder (CTE-35, Nanjing Ruiya). The temperature settings for each section of the extruder were 240 ℃，250 ℃，260 ℃，270 ℃，260 ℃，250 ℃，250 ℃，250 ℃. The die

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temperature was set to 275 °C, and the screw speed was 400 rpm. After granulation, the material was left to rest at 80 °C for 24 hours, then injection molded into tensile, impact test specimens and flat plates for further testing.

Table 1 Formula of PMMA/ASA used in this work

PMMA211 ratio	LP2068	MABS	1550F	1076	168
-	phr	phr	phr		
0.2	15	10 (758)	36	0.1	0.4
0.2	20	10 (920)	29	0.1	0.2
0.2	25	0	22	0.2	0.4
0.2	30	5 (758)	15	0.2	0.2
0.3	15	10 (920)	22	0.2	0.2
0.3	20	10 (758)	15	0.2	0.4
0.3	25	5 (758)	36	0.1	0.2
0.3	30	0	29	0.1	0.4
0.2	15	10 (758)	36	0.1	0.4
0.2	20	10 (920)	29	0.1	0.2
0.2	25	0	22	0.2	0.4
0.2	30	5 (758)	15	0.2	0.2
0.3	15	10 (920)	22	0.2	0.2
0.3	20	10 (758)	15	0.2	0.4
0.3	25	5 (758)	36	0.1	0.2
0.3	30	0	29	0.1	0.4

2.3 Testing

Mechanical properties testing: The tensile tests were conducted by a tensile tester (ZBC8400B) according to the standards GB/T 1042-2006 and GB/T 1843-2008, with the tensile test performed at a speed of 50 mm/min. The impact tests were conducted by a impact tester (GT-7045-MDL).

Heat resistance: The heat deflection temperature (HDT, 1.8 MPa) and Vicat softening temperature (VST, B50) were tested by.

Appearance properties: A color difference meter (X-RITE 7600) was used to analyze the color changes of the flat plates.

2.4 Data analysis:

The experimental data were analyzed using a Python program developed by the team, with the Pandas, scipy, and numpy libraries imported. The experimental results were evaluated in terms of the impact of each component on performance using range analysis and variance analysis.

Range analysis was performed by subtracting the minimum value from the maximum value in the data sample. The result, denoted as R in the figures, indicates that the larger the R value, the greater the influence of the factor on the performance. Variance analysis was performed using the following four-step procedure [16]:

(1) Calculate the total sum of squares of deviations:

$$SST = \sum (y_i - \bar{y})^2 \tag{1}$$

where SST is the sum of squares of deviations, yi represents the data points, and $\bar{y}$ is the mean value of the data set.

(2) Calculate the sum of squares of deviations for each factor:

$$SSA = \sum_{i=1}^{n} n_i(\overline{T_i} - \bar{y})^2 \tag{2}$$

$$MSA = \frac{SSA}{n-1} \tag{3}$$

where SSA is the sum of squares of deviations for factor A, and MSA is the mean square for the factor. n represents the number of levels of the factor, ni is the number of experiments at the i-th level, and $\overline{T_i}$ is the mean of the data at the ii-th level.

(3) Calculate the error sum of squares: The error sum of squares (SSE) and mean square error (MSE) are obtained by taking the minimum value from step (2).

(4) Calculate the F-value:：

$$FA = \frac{MSA}{MSE} \tag{4}$$

(5) Calculate the P-value from the F-distribution:

$$PA = P(F > FA) \tag{5}$$

This analysis was conducted using Python's scipy library. In the figures of this paper, each orthogonal analysis includes a P-value. When $P < 0.05$, it indicates that the P-value is smaller than the significance level, allowing for the rejection of the null hypothesis, which suggests that the conclusions drawn from the graph are statistically significant. In engineering practice, it is also generally accepted that when $0.05 < P < 0.1$, the factors are weakly correlated or marginally significant.

3 Results and Discussion

3.1 Mechanical Properties

The introduction of heat stabilizers and toughening agents is expected to affect the mechanical properties of the material. As shown in Figure 1, after the incorporation of various additives, the mechanical properties of the material system changed to varying degrees. LP2068, an ASA-type toughening agent, has a fine and uniform rubber phase, which causes the material's tensile strength to decrease from 63.3 MPa at 15 phr to 51.3 MPa at 30 phr (P=0.002), while the impact strength increases from 3.99 MPa at 15 phr to 8.04 MPa at 30 phr (P=0.002). MABS 758 and MABS 920 are two types of transparent ABS, and the experimental results show that both slightly decrease the tensile strength (P=0.014). The heat stabilizer 1550F has no effect on the mechanical properties of the material system ($P > 0.1$). It can be said that the changes in mechanical properties generally follow the pattern predicted by the mixing law.

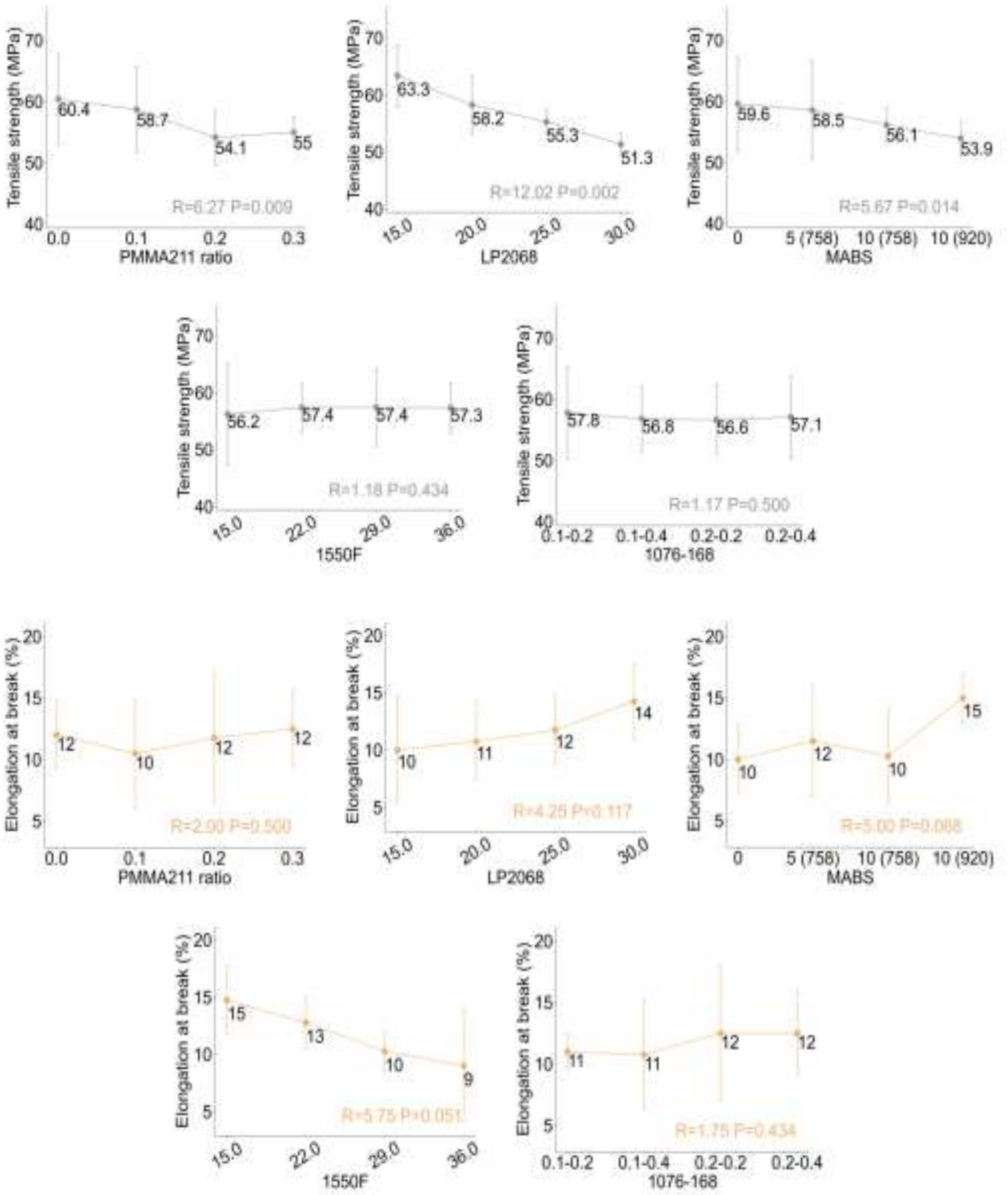


Figure 1 The formula vs. tensile properties

A significant conclusion arises from the addition of high-flow PMMA 211 to the system for PMMA-based materials, which has a notable impact on mechanical properties. When PMMA 211 was added at a proportion of 20%, the tensile strength decreased from 60.4 MPa to 54.1 MPa (P=0.009), while the impact strength increased from 4.64 to 7.24 (P=0.003). Compared to the slight decrease in tensile strength, the substantial improvement in toughness is undoubtedly a positive result.

To explore the true reason of this phenomenon, we conducted further verification experiments, as shown in Figure 3. We replaced the PMMA substrate with higher melt-flow PMMA 211 in both toughened and non-toughened systems. On one hand, the high-melt-flow PMMA substrate brought lower molecular weight segments, further leading to a decrease in the tensile properties of the substrate. However, when the replacement proportion was not high (ranging from 0 to 30%), this change was not significant. On the other hand, in terms of impact strength, there was almost no change in the non-toughened system, while in the toughened system, a similar trend to that shown in Figure 2 was observed. The impact strength increased from 2.54 to 3.04 kJ/m ²and then dropped back to 2.57 kJ/m ²

The difference in the high and low melt-flow ratio strategy in both toughened and non-toughened systems suggests that the toughening effect is likely due to the improved processability brought by a broader molecular chain range, which leads to more thorough plasticization and more uniform distribution of the toughening agent in the matrix. Essentially, this is a synergistic effect between the toughening agent and the matrix.

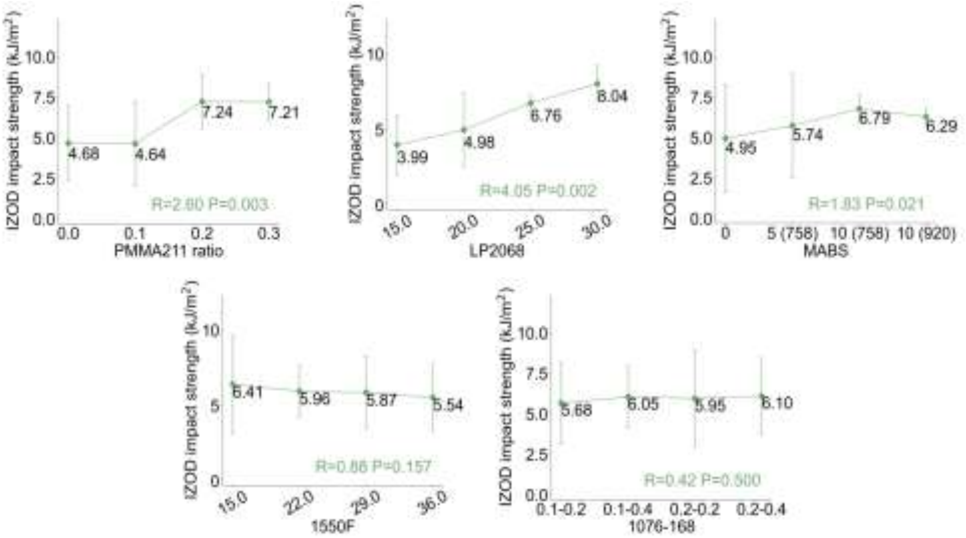
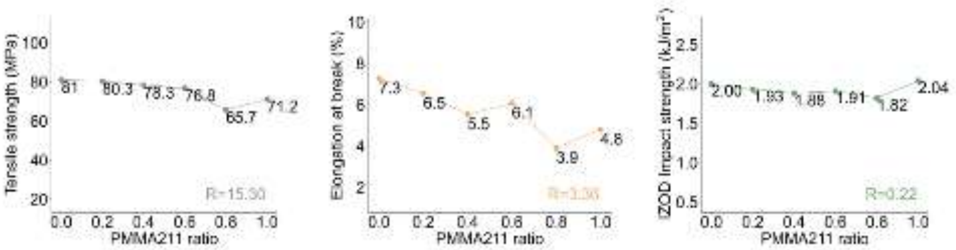
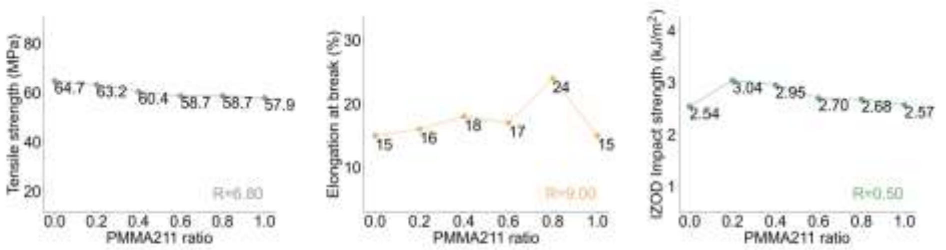


Figure 2 The formula vs. impact properties



Non-toughened



Toughened

Figure 3 High MFR PMMA vs. mechanical properties in toughened/ normal materials systems

3.2 Appearance

In terms of appearance, the impact of each formulation system on the material's visual characteristics is relatively minor. Here, we use the Lab color model for analysis. The model evaluates color in three dimensions: L represents brightness, where a higher L value indicates a brighter color; a represents the red-green axis, where a higher a value indicates more red, and a lower a value indicates more green; b represents the yellow-blue axis, where a higher b value indicates more yellow, and a lower b value indicates more blue.

Regarding the L value, apart from the proportion of PMMA211, other components in the formulation have minimal effect on the L value. As described in Section 2.1, the proportion of PMMA211 not only affects the L value but also shows similar trends in all color dimensions, reflecting the same changes as observed in mechanical properties. This further suggests that the high and low melt-flow PMMA strategy is beneficial not only for toughening agents but also for improving the uniformity and dispersion of colorants.

Additionally, due to the influence of the inherent color of the materials, other components also have some effect on the color of the material system. LP2068 increases both the a and b values, which is attributed to the conjugated structure of the rubber phase's double bonds. The addition of MABS slightly reduces the a and b values, as the conjugated structure of the styrene segments causes π-electron delocalization throughout the molecule, resulting in a slight blue shift. The addition of 1550F causes a significant decrease in the b value, which is due to the nitrogen-containing functional groups in the heat stabilizer.

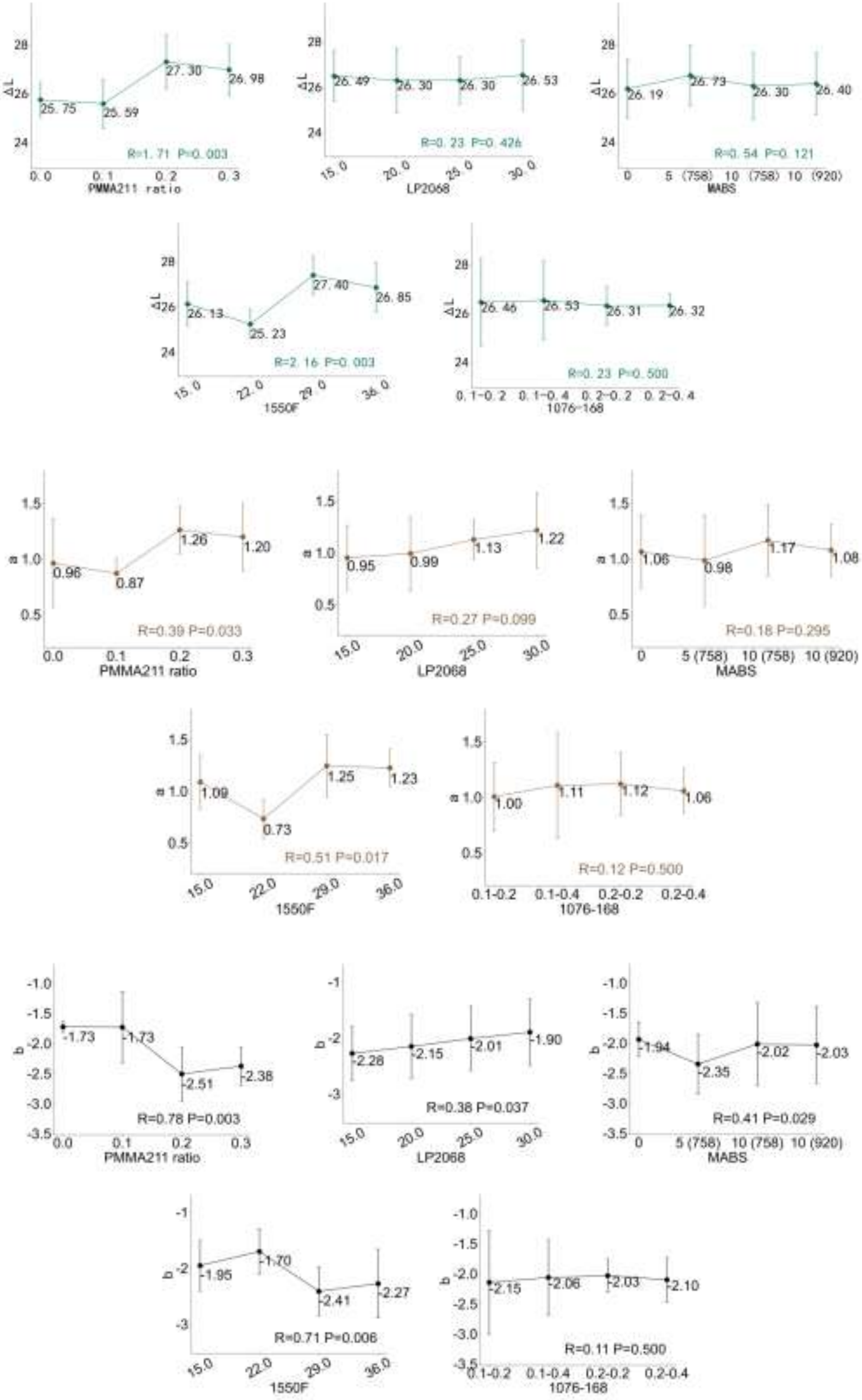


Figure 4 The formula vs. Color

3.3 Heat resisting properties

The heat resistance of the material system is evaluated using the HDT and VST. HDT focuses on assessing the material's serviceability under load, while VST is used to evaluate the material's thermal softening behavior and processing performance. The subtle differences between these two properties lead to slight variations in their response to the formulation system. LP2068 has a weak influence on both HDT and VST (P-values of 0.072 and 0.100, respectively). MABS has no effect on either property (P ＞ 0.1). As a heat stabilizer, 1550F significantly influences both HDT and VST, which is expected (P-values of 0.002 and 0.026, respectively).

It is worth noting that when the amount of 1550F is between 15 and 22 parts, there is a plateau in the increase of VST, whereas HDT does not show this plateau. This is because, under load conditions, HDT reflects the overall thermal state of the material, and its failure depends on the overall failure of the specimen, directly related to the total content of the heat-resistant component. However, VST is measured by a needle penetration test, which is more sensitive to the surface condition of the material. Specifically, when the amount of 1550F increases from 15 to 22 parts, the VST shows little change, indicating that the distribution of 1550F within the matrix is not uniform. With fewer components, 1550F tends to accumulate on the surface rather than within the matrix. When the heat stabilizer is added in larger amounts, it affects the interior of the matrix, and the VST starts to rise gradually once the critical concentration is reached.

This distinction in heat resistance performance also suggests the mechanism of the PMMA211 proportion. The proportion of PMMA211 has no impact on HDT (P=0.500), but in the more surface-sensitive VST, a noticeable decrease occurs at a 0.2 ratio, which mirrors the trend observed in mechanical properties and color changes (P=0.040). Clearly, we can infer that for surface-sensitive properties, such as mechanical performance, surface color, and VST, the high-low melt-flow blend strategy has a significant impact. However, for properties less sensitive to surface conditions, such as HDT, this strategy has little effect. The reason might be that during the injection molding process, the differences in flowability cause high melt-flow components to be more likely to be affected by fountain flow, moving to the surface. These high-flow components often carry more functionalized ingredients, further influencing the material's surface condition. Based on these findings, guidance can be provided for designing the surface characteristics of formulation systems.

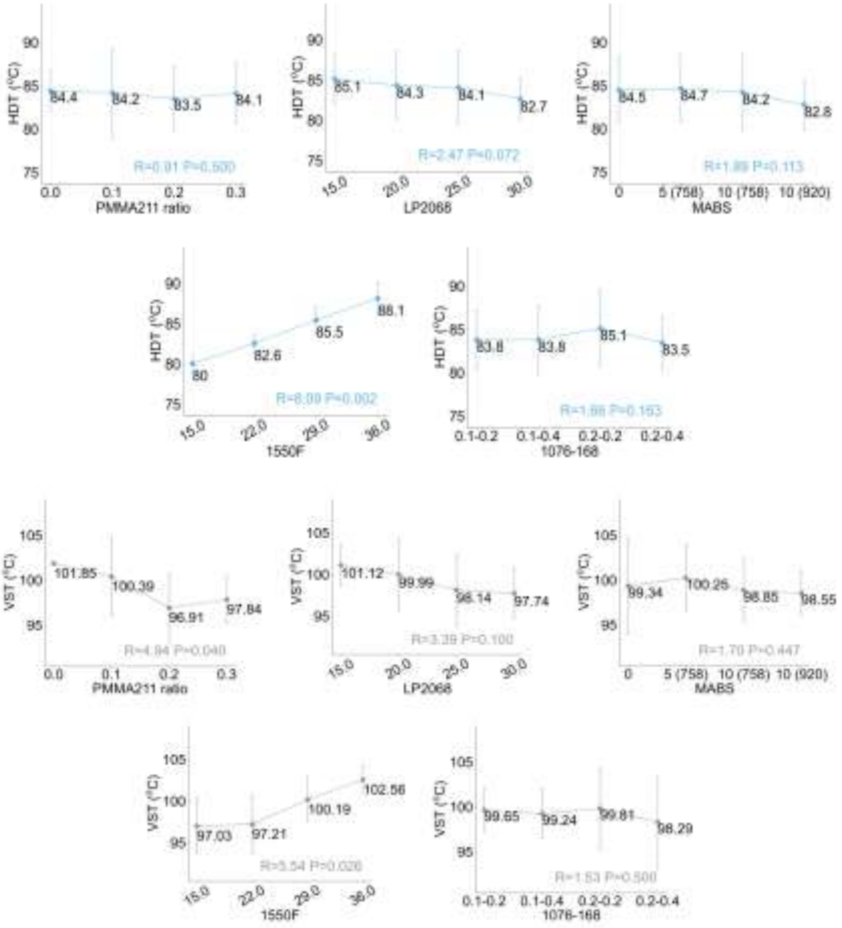


Figure 5 The formula vs. heat resistance properties

4 Conclusion

Orthogonal experiments were conducted to explore the impact of various formulation components on the overall performance of high-gloss black PMMA/ASA alloys. Hypothesis testing methods were used to assess the reliability of the experimental observations, and the following conclusions were drawn:

(1) Effect of Toughening Agents and Heat Stabilizers on Mechanical Properties: The introduction of toughening agents and heat stabilizers had different effects on the material's mechanical properties. LP2068, an ASA-based toughening agent, improved the impact strength by enhancing the uniformity of the rubber phase but caused a slight decrease in tensile performance. MABS 758 and MABS 920 had little impact on impact performance, but when added at higher ratios, they led to a decline in performance. The heat stabilizer 1550F had no effect on mechanical properties.

(2) Effect of PMMA211 on Mechanical Properties: PMMA211, as a high-flow material, had a significant impact on mechanical properties at a 20% ratio. While tensile performance slightly decreased, the impact strength significantly improved. Further verification experiments showed that PMMA211 improved the gradient distribution of the material, making the toughening agent distribution more uniform, which in turn enhanced toughness.

(3) Effect of Formulation on Appearance: The effect of the formulation on the material's appearance was minimal. Apart from the proportion of PMMA211, other components had little effect on the L value. The addition of PMMA211 aligned with the changes in mechanical properties, indicating that it not only improved toughness but also enhanced the uniformity and dispersion of colorants. Different additives had different effects on color: LP2068 increased both the a and b values, MABS lowered both a and b values, while 1550F significantly reduced the b value.

(4) Effect of Formulation on Heat Resistance: The formulation system had different effects on heat resistance, as measured by heat deflection temperature (HDT) and Vicat softening temperature (VST). LP2068 had a slight effect on both properties, while MABS had little to no effect. The heat stabilizer 1550F significantly improved both HDT and VST, particularly in the range of 15 to 22 parts, where a plateau in the VST was observed.

Effect of PMMA211 on Vicat Softening Temperature: PMMA211 had a notable effect on VST, especially at low ratios, causing a decrease in temperature. This change was consistent with the variations in mechanical properties and color. This phenomenon suggests a difference in the sensitivity of various properties to surface conditions. The high-low melt-flow blending strategy has a significant impact on surface properties but a minimal effect on intrinsic properties.

These findings highlight the importance of formulation components in tuning the surface and bulk properties of PMMA/ASA alloys, providing useful guidance for designing material systems with tailored performance characteristics.

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