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#### Article

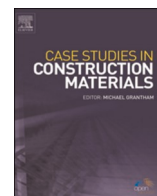
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# Investigation on the technical performance and workability of hot-melting road marking materials using for the high-altitude area

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## ABSTRACT

The special environment conditions in high altitude areas leads to serious cracking and peeling of road hot-melt marking coatings. In order to improve the durability of marking paint, a durable hot-melt marking paint was designed by modifying the paint with toughening-agent, rheological agent, and anti-aging agent. The modification mechanism of the modified coating was revealed through TG and FTIR analysis. The low-temperature anti cracking, adhesion, and anti-aging properties of the modified coating were studied by low-temperature bending test, interlaminar shear test and UV aging test. Besides this, the workability of modified coatings was tested onsite. The results showed that the mass loss rate of the rheological agent is 0.15% at 240 °C, the modified coating had good thermal stability within the mixing temperature range of the coating. There was no chemical change between the modifier and the coating, which was a physical blend. The modified marking paint had good fluidity, softening point and drying time, but its compressive strength was slightly reduced. With the increase of the content of the toughener, the low temperature crack resistance and adhesion of the marking coating gradually increase. When the toughener is 5%, the flexural tensile strain of the marking coating beam increased by 79.1%, and the adhesion strength of asphalt concrete increased by 53.4%. The anti-aging agent can shield most of the UV radiation and improve the anti-aging property of the coating by about 30%. The field process validation achieved the expected results. The modifier coating has excellent low temperature crack resistance, adhesion, UV aging resistance, and other properties, and has good application prospects in harsh environment areas.

## 1. Introduction

The function of road marking paint is to guide the driving of motor vehicles and non-motor vehicles on the road [1]. Relevant research shows that the correlation rate between road markings and traffic accidents is as high as 70%. At the same time, scientific and

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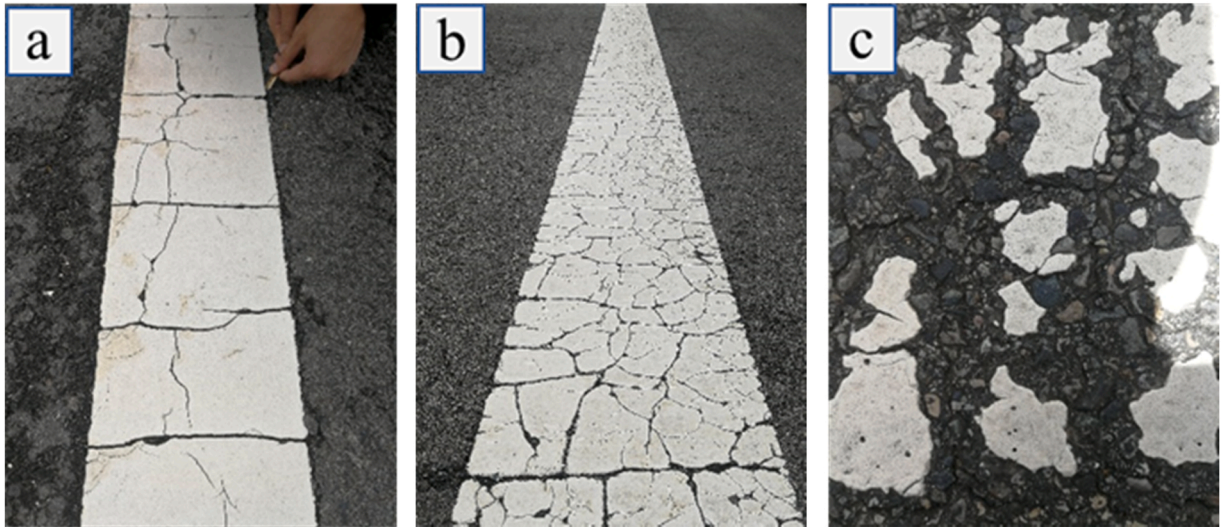
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**Table 1**  
Composition of hot melt road marking coatings.

Raw material	Type	Weight percentage
Synthetic resin	C5 hydrocarbon resin	about 14%
	Ethylene vinyl acetate resin (EVA)	about 1.5%~3%
Filler	Heavy calcium carbonate, talc	about 35%
	Quartz sand	about 35%
Pigment	Rutile titanium dioxide	about 3~8%
Plasticizer	Diethyl Phthalate (DOP)	about 1%
Lubricant	Polyethylene wax (PE wax)	about 1.5%
Reflective material	glass beads	about 15~23%



**Fig. 1.** Application status of high-speed hot melt type marking in Tibet, China (a. Net fissure; b. Cracking; c. Peeling).

reasonable marking design and layout can improve transportation efficiency by 30% [2,3]. With the rapid development of road infrastructure construction, the total mileage of roads is increasing, and a large number of markings need to be re-marked, re-marked and maintained on new roads and roads with preventive maintenance, repair maintenance and reconstruction. On the other hand, the number of cars is increasing year by year. It is effective to alleviate traffic congestion through traffic drainage, organization and channelization. The application of road marking adjustment, displacement and resurfacing in traffic engineering is becoming more and more common [4]. According to statistics, by 2022, the world's road marking paint market will reach \$ 5.35 billion [5].

Pavement marking according to the different coating composition, usually can be divided into: solvent type, hot melt type, two-component and water type, etc. [6,7]. At present, the hot-melt type is the dominant coating type. The hot-melt road marking coating is mainly composed of film-forming substances such as petroleum resin and rosin resin, and mixed with other pigments, filler and additives as secondary film-forming substances. The composition of hot-melt road coating is shown in Table 1 [8]. At room temperature is a powder, and then melted into a liquid by heating, after coating cooling film, premixed with a certain amount of glass beads to achieve continuous reflection [9]. It has the characteristics of short production cycle, low production cost, no pollution in the production process, good adhesion, no pollution to the environment after coating and short drying time [10].

However, as an organic material, the binder in the coating is susceptible to aging due to environmental factors such as temperature, oxygen, ultraviolet light and water during service, resulting in deterioration of the performance of the marking coating [11]. Especially in special areas, the service environment is more severe. The harsh environment leads to the cracking, peeling and loss of its functional characteristics of the markings, which not only affects the use of asphalt pavement, but also endangers the smooth flow of transportation and traffic safety. The typical cracking of road markings in high altitude areas (such as Tibet, China) is shown in Fig. 1.

At the initial stage of hot melt coating research, it was found that the coating was cracked, peeled off, easy to be polluted, etc. Researchers began to study the performance degradation mechanism from the perspective of coating formulation design [12]. The reason is that the main components of the road marking coatings are complex polymer organic materials, which are often subject to the influence of ultraviolet, heat, oxygen, and other environmental factors during the service process, resulting in irreversible aging reaction, resulting in reduced physical properties, such as hardening, embrittlement, loss of luster, bending deformation, crazing, cracking, mechanical properties decline, etc., thus affecting the service life of polymer materials [13,14]. This kind of coating is greatly affected by the temperature difference between day and night, and is prone to brittleness, cracking, overcurrent, and other problems, leading researchers to start from the coating formula to develop marking coatings that meet different environmental conditions.

**Table 2**  
Composition of original coating.

Ingredient Name	Weight percentage	Ingredient Name	Weight percentage
C5 resin	14%	Quartz sand	28%
Titanium dioxide	10%	Calcium powder (heavy calcium carbonate)	27%
glass bead	18%	Polyethylene wax	3%

**Table 3**  
Technical indicators of toughening agent.

Property	Results
Density (g/cm <sup>3</sup> )	0.875
VA content (%)	18
Thermal decomposition temperature(°C)	> 250
Softening point (°C)	82.0
Appearance	White transparent particles

Ludwig Eigenmann et al. [15] invented a kind of polymer resin, such as polyurethane and resin or polyethylene terephthalate resin, which embeds polymer cohesion on the coating surface. The added materials set up several sharp tips on the surface through adhesion, thereby improving visibility and providing wear resistance. Mirabedini [16] improved the performance of road marking coatings by optimizing the formulation of road marking coatings through mixed experimental design. The results showed that the mixed experimental design method scientifically provided the formulation of hot melt road marking coatings with excellent performance.

At present, vegetable oil has become an important modified monomer in resin synthesis. It is a popular direction for vegetable oil-modified marking coatings to extract components from vegetable oil to synthesize new bio-based polyols [17]. The advantage of vegetable oil-modified coatings is that natural vegetable oil contains a large number of unsaturated double bonds and can polymerize with resin monomers to achieve further chemical modification to obtain polyurethane products with better performance [18]. Yang [19] et al. synthesized hydroxyl tung oil-based non-ionic polyurethane dispersion by reacting hydroxyl in tung oil with 4,4 dicyclohexyl methane diisocyanate (HMDI). This dispersion can be used as a potential surfactant to improve the initial performance of marking coatings. Vikash Mishra [20] and others prepared a new waterborne UV curable polyurethane dispersion using castor oil, IPDI, DMPA, and HEMA as raw materials by acetone method. The results show that these new UV PUDs have application potential in coatings.

Coatings are a kind of polymer material with complex and diverse molecular structures, and molecular chains will break during oxidation [20,21]. In the oxidation resistance process of plastics, rubber, and other polymers, it is found that the addition of antioxidants and light stabilizers can effectively slow down the aging of polymers and prolong the service life of polymers [22,23]. Adding antioxidants and light stabilizers is the most universal, convenient, and economical method to improve the aging resistance of polymer materials, so it has been widely used [24,25]. At present, some scholars at home and abroad have applied antioxidants in the research of asphalt aging resistance and found that antioxidants have greatly improved the oxidation resistance of hydrocarbon compounds. Li [26] studied the impact of antioxidant types and formulations on asphalt anti-aging performance and found that antioxidants have greatly improved the anti-aging performance of hydrocarbon compounds and rubber, and the anti-oxidation effect of asphalt is greatly related to the types of asphalt and antioxidants. Ahmed and Li [27,28], etc., added UV absorber to the coating film and SBS modified asphalt, conducted the artificial accelerated aging test, and analyzed the aging resistance of the modified material by gel content and mechanical property test. The results showed that adding UV absorber could significantly improve the UV resistance of the coating film and asphalt. Tan, Mouillet [29,30], and other researchers found that the antioxidant did not significantly improve the ultraviolet aging resistance of asphalt, but had a good antioxidant effect on resin materials. Therefore, inhibitors such as antioxidants and light stabilizers can be added to the coating to reduce the degradation rate of coating performance and slow down the oxidation of binder.

In view of the serious cracking and falling off problems of hot-melt marking coatings at this stage, a durable hot-melt marking coating is designed and prepared by using toughening-agent, rheology-agent and anti-aging-agent modified coating to meet the needs of high-quality marking coatings in harsh environments and traffic. The modification mechanism of modified coatings was revealed through TG and FTIR analysis, and the technical properties of modified coatings were studied by flowability, low-temperature bending test, interlaminar shear test and ultraviolet aging test, and the field test section of the preferred modified coating was applied to verify the feasibility of its process and performance, which provided a theoretical and technical basis for the subsequent application of coatings.

## 2. Materials and test methods

### 2.1. Materials

#### 2.1.1. Coating materials

The original coating adopts the hot-melt road marking coating commonly used in China, and its components are shown in Table 2.

**Table 4**  
Technical indicators of rheological agent.

Property	Results
relative density(25 °C)	0.965
Saponification value (mg KOH/g)	182
Iodine value (mg(I <sub>2</sub> )/g)	85
Appearance	Light yellow oily liquid

**Table 5**  
Technical indicators of anti-aging agent.

Property	Results
MgO/Al <sub>2</sub> O <sub>3</sub> mol ratio	4.1
Average particle size(μm)	2
Specific surface area (m <sup>2</sup> /g)	35
Bulk density (g/cm <sup>3</sup> )	0.385
Appearance	White powder

**Table 6**  
Technical indicators of warm mixing agent.

Property	Results
Density (g/cm <sup>3</sup> )	0.906
Flash point	> 240
135 °C viscosity (Pa·s)	$5.62 \times 10^{-3}$
Appearance	White particles

**Table 7**  
Proportion of modified ingredient.

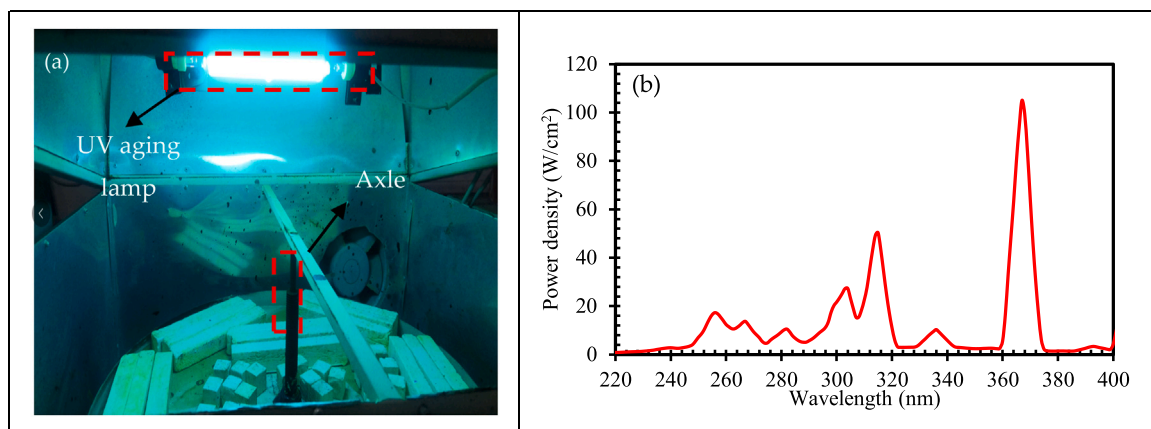
NO	Toughener toughening agent (%)	Rheological agent (%)	Anti-aging agent (%)	Warm mixing agent (%)
Original	0	0	0	0
3%T + A	3	2	1	1.5
5%T + A	5	2	1	1.5
7%T + A	7	2	1	1.5
5%T	5	2	0	1.5

### 2.1.2. Modifier

The modified material of marking coating consists of toughening agent, rheological agent, anti-aging agent and warm mixing agent. The toughening agent has excellent low temperature resistance. With the increase of molecular weight, its softening point increases, its processability and the surface gloss of the test piece decrease, but its strength increases, impact toughness and environmental stress cracking resistance improve. Table 3 is the technical indicators of the toughening agent; Rheological agent has the effect of cold resistance and plasticization, which can improve the plasticity and low-temperature crack resistance of the coating while increasing the fluidity. Table 4 is the technical indicators of rheological agent; The anti-aging agent plays the role of shielding and absorbing ultraviolet rays, improving the durability of the marking. Table 5 is the technical indicators of anti-aging agent; warm mixing agent can reduce viscosity at high temperature and increase viscosity at low temperature, which can reduce coating application temperature and improve construction workability and viscosity toughness. Table 6 is for technical indicators of warm mixing agent.

### 2.2. Preparation of modified marking paint

The modified is a hot-melt road marking coating which was divided into two stages. The first stage was the melting of the original paint, the heating temperature was 160 °C, and the low-speed mixing at 300 r/min was adopted, with a duration of about 2 min. The second stage was the modifier feeding stage, where all modifiers were added, the heating temperature was 200 °C, the high-speed mixing stage of 1000 r/min was adopted, and the duration was about 8 min. At the initial stage of mixing, the particles which suspended in the surface was stirred until the suspended particles disappeared completely, and the hot-melt coating and the modified ingredients had been mixed evenly. Table 7 is the proportion of modified ingredients.



**Fig. 2.** Ultraviolet aging test (a: Ultraviolet aging process; b: The UV lamp's spectral emission).

### 2.3. Chemical composition analysis of modified marking paint

#### 2.3.1. Thermogravimetric analysis

The thermal stability of the rheological agent was tested by synchronous thermal analyzer (TG). The thermal weight loss (TG) of the sample was analyzed by STA449F3 comprehensive thermal analyzer produced by NETLSCH. The thermal stability of coating is characterized by heating coating at a certain heating rate and continuously testing its quality change data. The heating range is 30–600 °C, and the heating rate is 10 °C/min.

#### 2.3.2. Chemical composition analysis

Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR) was used to detect the functional groups of the original and modified coatings. The asphalt sample is irradiated by infrared rays of different wavelengths to form a specific spectrum. The main sample preparation methods used in this study are as follows: put the prepared coating into the analyzer for infrared spectrum test at 4000 – 600  $\text{cm}^{-1}$  wave number.

### 2.4. Physical property test of plants

#### 2.4.1. Liquidity test

The fluidity of the original coating and the modified coating is tested by the fluidity method. The standard coating test cup is used for the test, and the temperature is 200 °C. The main steps are as follows: first, heat the fluidity measuring cup to about 200 °C and keep it for 1 h; Fill the measuring cup with the hot melt coating to be tested, open the outflow port and record the time. The time when the paint runs out is the fluidity.

#### 2.4.2. Softening point test

The softening point of the original coating and the modified coating is tested by the ring and ball method. The test liquid is glycerin, and the heating rate is 5 °C/min. Fig. 2 is comparison before and after the test.

#### 2.4.3. Gross bulk density test

The coating into was injected the cavity of the sample preparer made of Q235 steel, whose size is 20 mm × 20 mm x20 mm, and cool it to room temperature. Use a slightly heated scraper to cut off the protruding part of the end surface. Prepare 3 test blocks for each group. After being placed for 24 h, vernier caliper was used to measure the length, width and height of the test block (accurate to 0.01 mm), and a balance was used to weigh the mass of the test block (accurate to 0.01 g). Calculate the average density.

#### 2.4.4. Drying time test

The drying time of the coating shall be tested with the non-sticking time tester for road marking coating meeting the requirements of JT/T 996. After the paint was coated, immediately press the stopwatch to start timing. After 1 min, roll the tester from the center of one end of the coating plate to the other end for 1 s every 10 s. Observe whether the tester's tire is sticky.

### 2.5. Tracer paint pavement performance test

#### 2.5.1. Three-point bending test

Using three-point bending test (low temperature bending test), forming the reticle coating trabecular, – 10 °C after holding for 4 h, the low temperature bending test, the size of the trabecular is 170 × 23 × 20 mm, the height h is 23 mm, the width is 20 mm, the span



L is 120 mm, the test temperature is  $-10^{\circ}\text{C}$ , and the loading rate is 5 mm/min. The following Eqs. (1)–(3) are used to calculate the maximum bending tensile strain and bending stiffness modulus of the trabecula.

$$R = \frac{3 \times L \times P}{2 \times b \times h^2} \quad (1)$$

$$\varepsilon = \frac{6 \times h \times d}{L^2} \quad (2)$$

$$S = \frac{R}{\varepsilon} \quad (3)$$

Where, R—bending tensile strength(MPa),  $\varepsilon$ —Maximum bending tensile strain( $\epsilon$ ), S—bending stiffness modulus(MPa), P—maximum load when the specimen is broken(N), d—mid span deflection of the test piece when the ring is broken(mm).

### 2.5.2. Cube compressive strength test

The mechanical properties of coating mucilage were studied by the compressive strength test of  $23^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  cube blocks. The specimen size is  $20\text{ mm} \times 20\text{ mm} \times 20\text{ mm}$ . Place the specimen in an environmental box at  $23^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  for more than 4 h to ensure the uniform temperature of the specimen. Universal testing machine (UTM)—100 is used as the test equipment, and the loading rate is 30 mm/min.

### 2.5.3. Interlayer shear test

Due to the mechanical and chemical effects caused by snow removal in Tibet, the markings are easy to fall off due to insufficient interlayer viscosity, so the adhesion strength between the marking paint and the pavement is an important indicator for evaluating the modified markings. In this study, interlaminar shear test was used to evaluate the adhesion of linear coatings to pavement. The sample adopts AC-13 matrix asphalt concrete base and cement concrete base with a diameter of 100 mm and a thickness of 40 mm, and the upper layer is poured with about 30 mm marking paint to facilitate testing its interlaminar shear strength. Universal testing machine (UTM-100) is used for the test, the test temperature is  $23^{\circ}\text{C}$ , and the loading rate is 5 mm/min. The interlayer shear strength is calculated by Formula (4).

$$R_B = \frac{P_B}{A} \quad (4)$$

Where,  $R_B$ —Interlayer shear strength (MPa),  $P_B$ —maximum load in case of interlayer breakage (N), A—bonding area between layers ( $\text{mm}^2$ ).

### 2.5.4. Ultraviolet aging test

Artificial accelerated weathering test is used to study the aging resistance of the coating. The test temperature is  $63^{\circ}\text{C}$ , the test time is 600 h, and the total radiation energy of the test is about  $2.3 \times 10\text{ kJ/m}^2$ . Three aging specimens in each group are used to test the compressive strength, maximum bending tensile strain and bending stiffness modulus of the beams after aging. The ultraviolet aging is shown in Fig. 2.

## 2.6. Working performance test

### 2.6.1. Overview of the test road

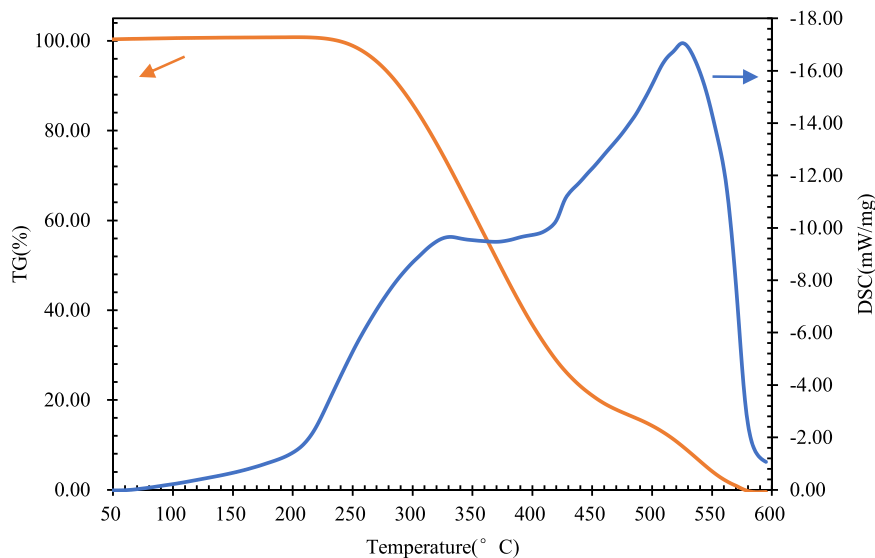
It can be seen from the indoor test results that the comprehensive performance of 5% T + A modified coatings is the best, so the on-site process validation was carried out for this group of formulations. The hot melt coating used in this process validation was the same batch of coating used in the maintenance and construction of expressway on the same day. Considering that it is only for process validation rather than performance validation, in order to avoid the possible adverse impact on the normal maintenance and subsequent performance of the expressway, the base plane of process validation is not selected on the expressway main line. This process verification was near interchange where expressway intersect. One of the base surfaces is the cement concrete pavement of the internal road of Asphalt Mixing Station on expressway. The cement concrete pavement markings were drawn near the scale, with a total of three solid lines, each of which is 5.2 m long and 25 cm wide. In order to form a sufficient thickness and provide a deceleration prompt for the transporter, each marking is composed of three layers of materials stacked and marked in three times. The second base surface is the asphalt concrete pavement of interchange ramp. The asphalt concrete base surface modified marking line is laid along the old marking line. The width of the solid line is 20 cm, the thickness is 2 mm, and the length of the straight and curved sections is 35 m in total.

### 2.6.2. Field sampling

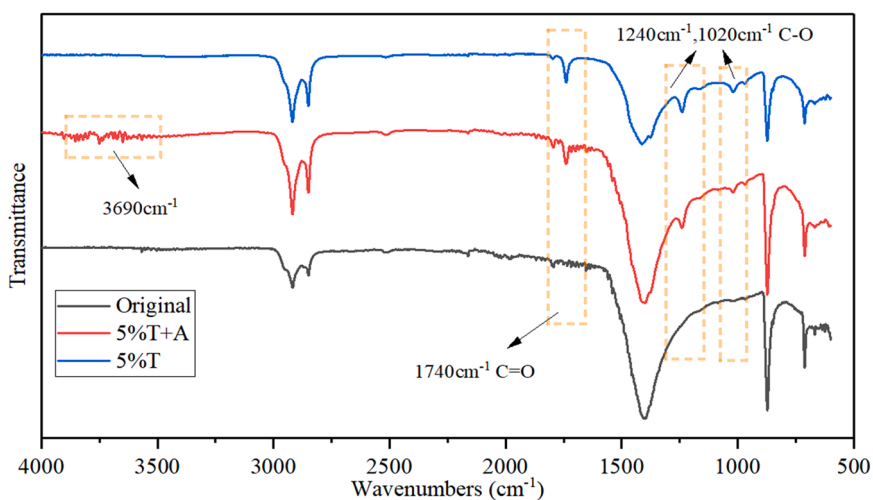
In order to verify the performance of the paint prepared by the on-site process, after the modified coating was mixed in the kettle and unloaded to the scribing machine, the casting mol is sampled from the flow outlet of the scribing machine, and the performance test verification was carried out after the molding. Table 8 is sampling parameters,

**Table 8**  
Sampling Parameters.

Test item	Sample size	Number of samples
Softening point	diameter 9.53 mm	2
Compressive test	20 mm × 20 mm × 20 mm	6
Crack resistance test	170 mm × 23 mm × 20 mm	3



**Fig. 3.** TGA/DTG curve.



**Fig. 4.** FTIR diagram of original paint and modified coating.

### 3. Results and discussion

#### 3.1. Study on modification mechanism of modified marking paint

##### 3.1.1. Thermal stability of marking paint

After being added with the toughening agent, the impact toughness and environmental stress cracking resistance of the coating were both improved, meanwhile, due to the lower thermal decomposition temperature which was about 240 °C [31]. With the increase of molecular weight, its softening point increases, and its processability and surface gloss of the test piece decrease. Therefore, it



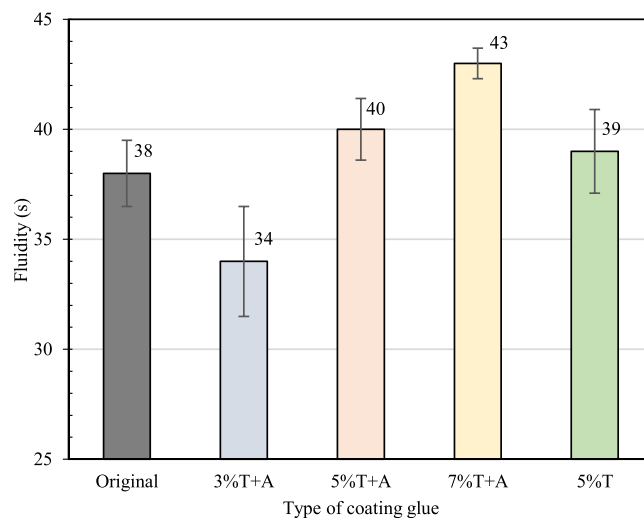


Fig. 5. Fluidity of each coating.

is necessary to add rheological agent to improve its workability. The rheological agent which is vegetable oil has good compatibility with polymer copolymers such as resins and plastics, and to improve the plasticity of the paint as a plasticizer. The addition of rheological agent in the coating may cause the instability of the mixing of the two. Therefore, in order to study its thermal stability, thermogravimetric analysis was carried out for the rheological agent. As Fig. 3 is shown that the thermal mass loss of rheological agent is divided into three parts: the first part is 30 – 240 °C, the mass loss rate of rheological agent is 0.15%, basically unchanged, and the temperature range has constructability; The second part is 240 – 360 °C, the mass loss rate of rheological agent is more than 50%, and most of the light components in the rheological agent have volatilized; The third part is 360 – 480 °C, the mass loss rate is more than 80%, and most of the rheological agents have been decomposed and volatilized. The results show that the rheological agent will not decompose and volatilize in the melting temperature range of 180 – 240 °C, and has good thermal stability.

### 3.1.2. Chemical composition

In order to reflect the change of chemical composition of the modified coating, the original, 5% T and 5% T + A coatings were analyzed by FTIR. The analysis results are shown in Fig. 4. It can be seen from Fig. 4 that the main functional groups of the three kinds of paints are as follows: the double peaks near 2900  $\text{cm}^{-1}$  are caused by the antisymmetric and symmetric stretching vibration of alkane  $\text{CH}_2$  and its derivatives, indicating that there are more long-chain alkanes in the paint; 1440  $\text{cm}^{-1}$  is the absorption peak superposed by  $\text{CH}_2$  bending vibration and  $\text{CH}_3$  asymmetric bending vibration of alkanes; 870  $\text{cm}^{-1}$  is the absorption peak caused by the out of plane bending vibration of benzene aromatic CH; 720  $\text{cm}^{-1}$  is the absorption peak caused by the plane swing of alkane  $\text{CH}_2$  [32]. Compared with the original paint, the 5% T and 5% T + A pastes have increased three obvious infrared absorption peaks of 1740  $\text{cm}^{-1}$ , 1240  $\text{cm}^{-1}$  and 1020  $\text{cm}^{-1}$ . 1740  $\text{cm}^{-1}$  is caused by the expansion vibration of C=O, and 1240  $\text{cm}^{-1}$  and 1020  $\text{cm}^{-1}$  are caused by the expansion vibration of C-O, indicating that vinyl acetate is added into the pastes. Compared with the original coating and 5% T, a new infrared absorption band appears near 3690  $\text{cm}^{-1}$  for 5% T + A glue, which is caused by the stretching vibration of free hydroxyl groups on the surface of LDHs laminates. It can be seen that the original coating and the modified coating have a high consistency on the absorption peak, the composition of the main functional groups is very similar [33,34], and the new absorption peak also indicates the addition of the modifier. This shows that the preparation of durable marking paint is mainly physical blending, without chemical change.

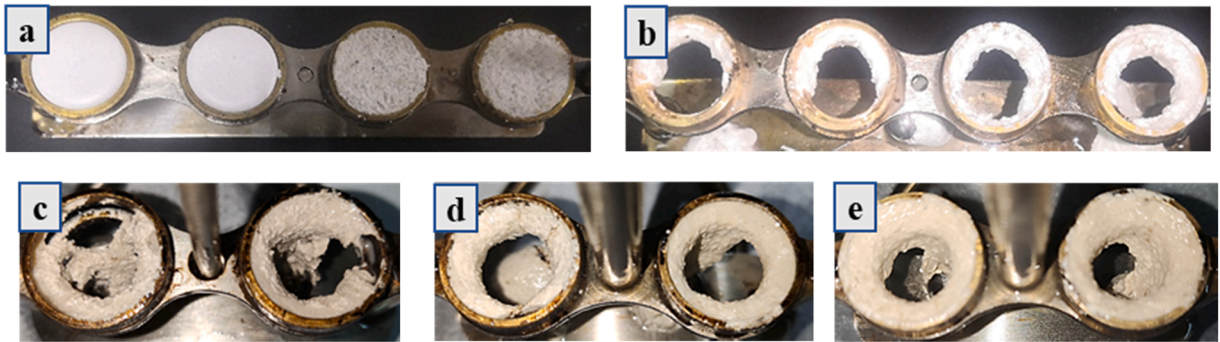
## 3.2. Study on the physical properties of modified marking coatings

### 3.2.1. Fluidity

The fluidity is a key indicator of the working performance of the marking paint, and its excellent workability must be guaranteed when the marking paint is modified. The flow test results of the original coating and modified adhesive is shown in Fig. 5. It can be seen from Fig. 5 that the fluidity of the original coating and the modified coating meet the requirements of specification 35–45 s. As the toughening agent will increase the viscosity and toughness of the coating, the viscosity of the coating will increase and the fluidity will gradually decrease with the increase of the amount of the toughening agent. The fluidity of 3% T + A is the smallest and smaller than that of the original coating, because the addition of rheological agent increases the light components in the mortar, which leads to good compatibility between the toughening agent and the binder in the coating, and improves the plasticity of the coating. The addition of additives can reduce the viscosity of the coating at high temperature and increase the viscosity at low temperature, so that the modified coating has a more appropriate construction fluidity. The test results show that the modified paint has good workability. (Table 9).

**Table 9**  
Softening point of each paint.

Type of mixture	Softening point of global method (°C)		Average value (°C)
	1	2	
Original	111.3	113.5	112.4
3%T + A	103.91	103.63	103.77
5%T + A	106.82	107.45	107.14
7%T + A	108.01	107.68	107.85
5%T	107.21	109.35	108.28
Specification requirements	90–125		



**Fig. 6.** Comparison diagram before and after softening point test (a: Before the test; b: Original; c: 3%T + A; d: 5%T + A; e: 7%T + A).

**Table 10**  
Density of each paint.

Type of mixture	Cubic (20 *20 *20 mm) block mass (g)				Gross bulk density (g/cm <sup>3</sup> )
	1	2	3	Average	
Original	15.6	15.7	15.4	15.6	1.95
3%T + A	16.6	16.3	16.4	16.4	2.05
5%T + A	15.6	15.7	15.4	15.6	1.95
7%T + A	14.9	14.9	15.0	14.9	1.87
5%T	16.1	16	15.8	16.0	2.00

### 3.2.2. Softening point

The sample before and after softening point test are shown in Fig. 6. The softening point test results of the original coating and modified adhesive is shown in Table 10. As can be seen from Fig. 6, due to the presence of 35% filler in the marking paint, it is different from the thin film coating, similar to the asphalt mortar, and the surface of the softening point sample was relatively rough after leveling [18,35]. After the coating reaches the softening point, due to the poor ductility, a cavity directly appears in the middle of the sample, and the steel balls directly fall off instead of being wrapped by mucilage; and after the asphalt mucilage reaches the softening point, the wrapped steel balls generally fall off, with the increase of the viscosity-toughness of asphalt binder, the smaller the cavity of the sample is after the steel ball falls off [28]. It can be seen from Fig. 6e that a large cavity appeared in the middle of the unchanged coating sample, and its viscosity was relatively poor. However, with the increase of toughener content, the smaller the cavity is in the coating softening point sample after the steel ball falls off. The appearance of 7%T + A group has been similar to that of ordinary asphalt binder after the test, and has a good viscosity and toughness. It is verified from the side that the toughening agent can increase the viscosity-toughness and ductility of the coatings [36].

As can be seen from Table 10, the softening point of the original coating and the modified mortar of both meet the requirements of the specification of 90–125 °C, and the softening point of the original coating is the largest. The rheological agent is non-drying liquid vegetable oil, which would increase the rheological property of the coating and reduced the softening point by about 8 °C with the addition of additives such as rheological agent and toughening agent. As the flexibilizer has good flexibility and elasticity, the viscosity increases with the increase of its molecular weight or content, and its softening point slightly increases. Since both the toughening agent and the auxiliary agent can increase the viscosity at about 110 °C, although the softening point of the toughening agent is only 82 °C, the softening point gradually stabilizes at about 108 °C with the increase of the content of the toughening agent.

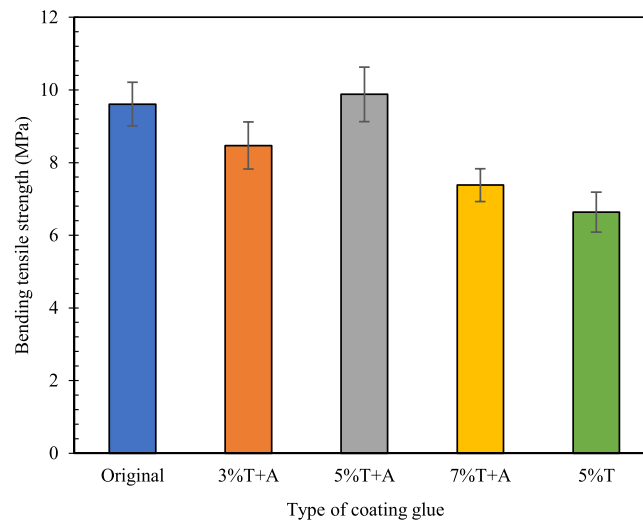
### 3.2.3. Density

The cured volume and density of the coating is a common indicator to measure the working performance and road performance of

**Table 11**

Drying time of each paint.

Type of mixture	The drying time of non-stick wheel (s)		Average value (s)
	First time	Second time	
Original	60	70	65
3%T + A	80	70	75
5%T + A	80	90	85
7%T + A	100	90	95
5%T	90	110	100
Specification requirements	< 180 s		

**Fig. 7.** Bending tensile strength of various coatings.

the marking coating, which reflects the density of the coating curing. The specification requirements range off 1.8–2.3 g/cm<sup>3</sup>. The cured volume density of the five coatings is shown in Table 10. It can be seen from Table 10 that the density of the modified coating is similar to that of the original marking. As the density of the modifier is far less than that of the original coating, the density of the modified coating gradually decreases with the increase of the modifier content. However, the density of 3% T + A, 5% T + A and 5% T is not less than the original sample, indicating that the modified coating is denser after curing, the less internal porosity [37,38]. Which is due to the better compatibility of the coating due to the addition of rheological agents and additives. The results show that the modified coating has better compactness and workability.

#### 3.2.4. Drying time

The drying time of non-stick wheel is an important indicator of the construction workability of marking paint, which reflects the maintenance and opening time of road marking after construction. For roads, the amount of drying time that the marking paint is applied to the road surface has a significant effect on road closure congestion. The longer the drying time, the greater the impact on road traffic. On the contrary, the shorter the drying time, the smaller the impact. The drying time of non-stick wheel for hot-melt road marking is required to be within 3 min, ensuring the road opening time to be about 15 min [10]. Drying time of nonstick wheel of coating is shown in Table 11. The drying time of non-stick wheel is mainly affected by the viscosity of the coating. When the temperature of the coating is reduced, the viscosity is reduced, and the adhesion with the rubber wheel is weakened gradually. Finally, the wheel is completely non-stick.

As can be seen from Table 11, rheological agent, toughening agent and additives all play the role of increasing viscosity. With the addition of modifier, the viscosity of the coating increases, the rate of viscosity decrease slows down, and the time required for the coating not to stick to the wheel increases, it increased from 65 s to about 95 s, but the drying time was much less than 180 s. Therefore, it demonstrates that the modified coating has better bonding performance and does not affect the opening time of the road after coating.

### 3.3. Study on road performance of modified marking paint

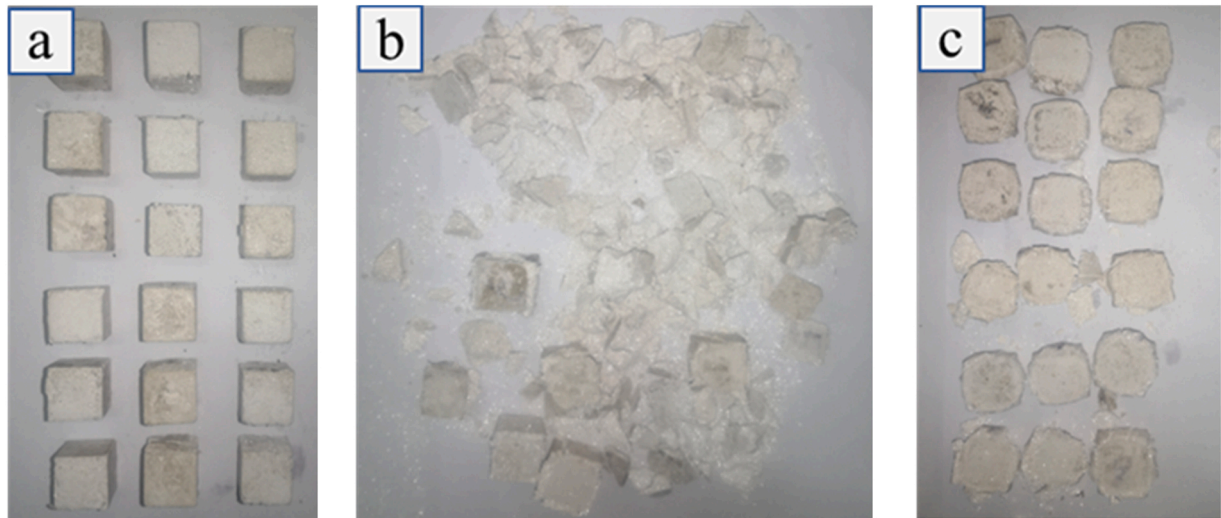
#### 3.3.1. Low-temperature performance

The low-temperature crack resistance of four kinds of modified marking coatings and the original samples was studied by three-

**Table 12**

Low temperature bending test results of various coatings.

Type	Category maximum breaking force (N)	Bending tensile strength (MPa)	Maximum bending tensile strain ( $\mu\epsilon$ )	Modulus of flexural stiffness (MPa)
Original	565.1	9.61	3354.17	2866.34
3%T + A	428	8.47	5558.33	1524.30
5%T + A	481	9.88	9362.50	799.57
7%T + A	434	7.38	12841.67	574.98
5%T	390	6.64	8050.00	824.24

**Fig. 8.** Compressive sample diagram (a. before test; b. after 23 °C; c. after 50 °C).

point bending test. The bending tensile strength and three-point bending tensile results are shown in Fig. 7 and Table 12. According to the three-point bending-tension test, the greater the bending-tension strain, the stronger its deformation resistance, and the lower the bending stiffness modulus, the stronger its bending resistance, and the better the low-temperature crack resistance of marking coatings. The three-point bending process of coating mucilage is similar to that of asphalt mucilage. The maximum breaking force of asphalt mucilage under low temperature is about 400 N and the flexural strength is 8 MPa [36]. The flexural tensile strength of the coating trabecular for pavement marking shall be appropriate to that of the asphalt material for pavement. The flexural tensile strength shall be around 8 MPa, high or low flexural tensile strength may lead to low-temperature cracking due to incompatibility with pavement [39].

It can be seen from Fig. 7 that the modifier is mainly a polymer compound, which will improve the flexibility of the coating. When the content is too high, it will reduce the strength of the material, resulting in the decrease of the maximum breaking force of the coating trabecular, but the addition of the modifier will make the coating more dense. Therefore, with the increase of toughening agent, the Bending tensile strength of the modified coating trabecular first increases and then decreases, and the 5%T + A Bending tensile strength is 9.88 MPa higher than that of the original coating, and is similar to the low-temperature flexural tensile strength of the asphalt material. Due to the excellent low-temperature resistance of the toughening agent, its molecular weight increases with the increase of the amount of the toughening agent, and the impact toughness and environmental stress cracking resistance of the coating are improved [40]. It can be seen from Table 12 that compared with the original coating, the bending tensile strains of 3% T + A, 5% T + A and 7% T + A modified coatings increased by 65.7%, 179.1% and 282.9% respectively, and the bending stiffness modulus decreased by 46.8%, 72.1% and 79.9% respectively. The test results show that the toughening agent can greatly enhance the low temperature anti cracking performance of the marking paint, and improve the low temperature anti cracking performance by more than 50%.

### 3.3.2. Compressive strength

The compressive strength requirements of road marking paint are 23 °C condition is not less than 12 MPa, 50 °C condition is not less than 2 MPa. There is more than 30% filler in the marking paint, which is the main stress skeleton in the process of compression [6]. Excessive addition of high molecular materials will lead to a decrease in the content of fillers such as quartz sand in the marking paint and a slight decrease in the compressive strength of the paint. Therefore, the basis of elastic-plastic modification of marking paint, it is also necessary to ensure that the mechanical properties (cube compressive strength) of marking paint do not decrease significantly. The compressive strength tests at 23 °C and 50 °C were carried out on five kinds of coating cubes. Test samples and test results are shown in Fig. 8 and Fig. 9. It can be seen from Fig. 8 that the coating test block at 23 °C mainly suffers from brittle fracture, while plastic fracture

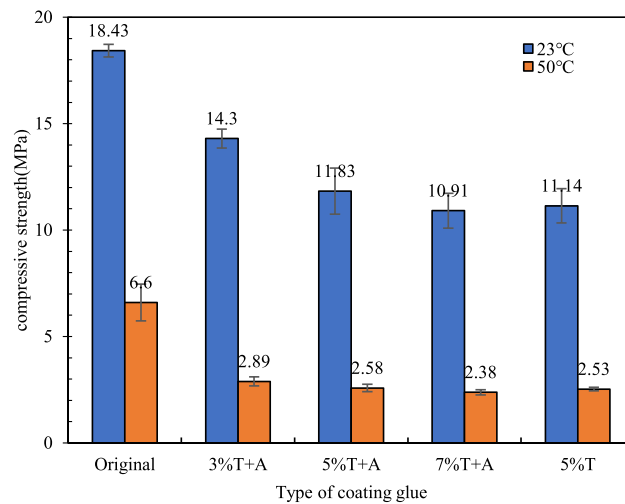


Fig. 9. Compressive strength of various coatings.

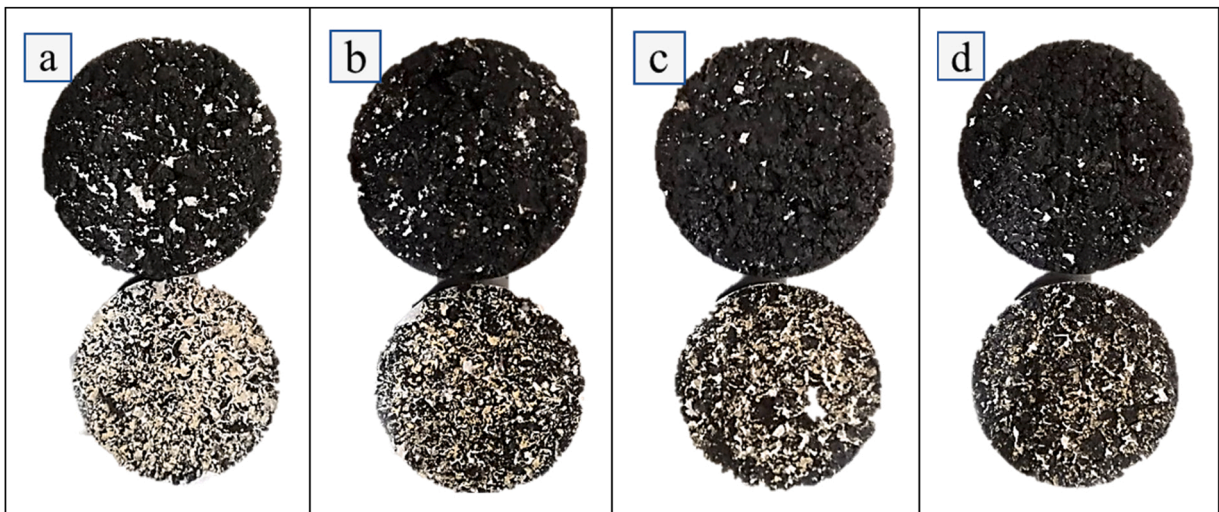


Fig. 10. Interlayer Shear Interface between Asphalt Pavement and Paint (a. Original, b. 3%T + A, c. 5%T + A, d. 7%T + A).

occurs at 50 °C. It can be seen from Fig. 9 that under the condition of 50 °C, with the increase of modifier, the compressive strength decreases gradually, but they are all greater than 2 MPa. Although the addition of modifier will lead to a decrease in the compressive strength of the marking paint, the decrease in the compressive strength of the marking paint is not large in the modification group. Due to the addition of toughener, the toughness of the coating increases, the stiffness decreases, and the strength decreases [35]. With the increase of modifier, the viscosity-toughness of the coating increases, the stiffness decreases, and the compressive strength decreases gradually. The compressive strength of the coating with high content of toughener at 23 °C is slightly lower than the specification requirements. The compressive strengths of 5%T + A and 7%T + A are 1.4%, 9.1% and 7.2% lower than the 12 MPa required by the specification. Under the actual service conditions, the coating thickness of marking paint is 2–3 mm, and no compression rupture occurs. The general rupture forms are shedding and cracking. The requirement on compressive strength can be slightly relaxed [10]. Therefore, the compressive strength slightly lower than 12 MPa has little effect on the road performance.

### 3.3.3. Adhesion between layers

#### (1) Adhesion of asphalt pavement marking paint.

The interlaminar shear interface between AC-13 matrix asphalt concrete and coating is shown in Fig. 10, the test load displacement process is shown in Fig. 11, and the interlaminar shear strength is shown in Table 13. It can be seen from Fig. 10 that there are many white coatings left on the asphalt concrete section after shearing between the original coating layers, and the interlaminar damage mainly occurs at the coating interface; However, with the increase of the toughening agent, the residual paint on the asphalt concrete section gradually decreases, the residual asphalt mortar on the marking paint section increases, and the broken interface gradually



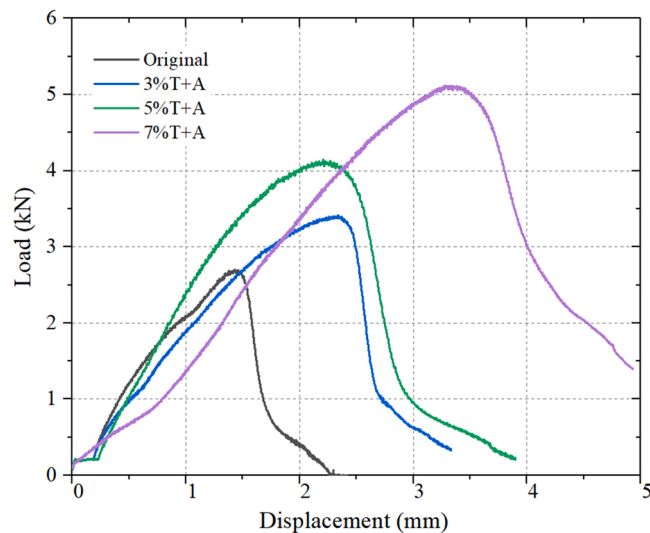


Fig. 11. Interlayer shear load displacement diagram.

**Table 13**

Shear strength between coatings and asphalt layers.

No	Maximum load (kN)	Position corresponding to the maximum load (mm)	Interlayer shear strength (kPa)
Original	2.70	1.45	344.00
3%T + A	3.28	2.45	417.87
5%T + A	4.14	2.34	527.65
7%T + A	5.12	3.34	651.57

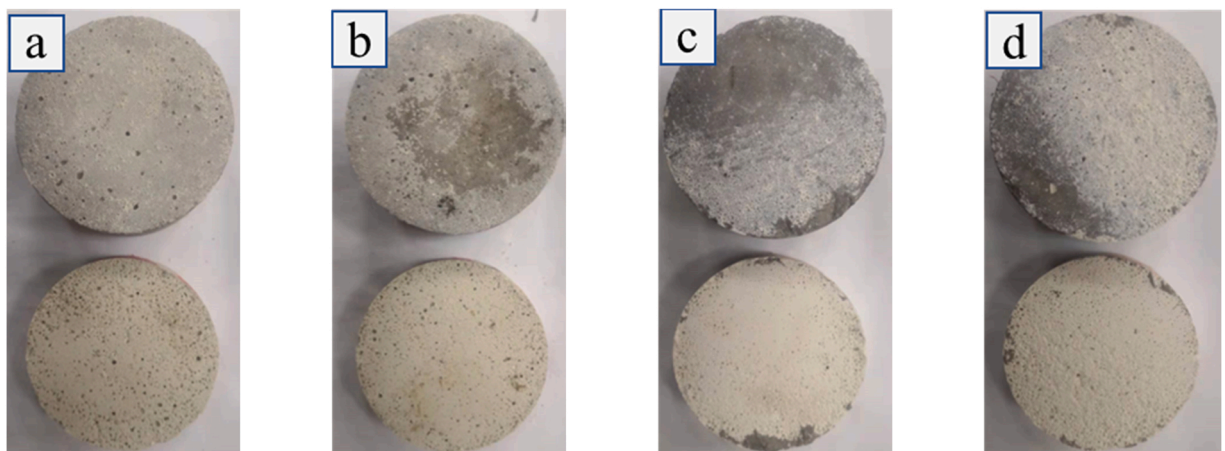


Fig. 12. Interlayer shear interface between cement pavement and coating (a. Original, b. 3%T + A, c. 5%T + A, d. 7%T + A).

changes from glue coating mortar to asphalt mortar. It shows that with the increase of toughening agent, the viscosity and toughness of the modified coating are enhanced, and its cohesion and adhesion to asphalt mortar are gradually higher than those of asphalt mortar. It can be seen from Table 13 that with the increase of toughening agent, the interlayer shear strength between the coating and asphalt pavement increases. Compared with the original coating, the interlaminar shear strength of the modified coating with 3% T + A, 5% T + A and 7% T + A increased by 26.21%, 53.38% and 89.41% respectively. The cracking of asphalt pavement material is mainly due to the difference of cohesion and adhesion of cementing material. When the cohesion of cementing material is greater than the adhesion, cracking and breaking will occur at the adhesion interface. When the adhesion is greater than the cohesion, cracking and breaking will occur inside the cementing material [41]. AC-13 matrix asphalt concrete interlayer shear strength is generally 500 kPa, when marking paint adhesion is less than the shear strength of asphalt concrete, marking off will occur [42]. The results show that when the content of toughener is more than 5%, the interlayer shear strength of marking paint and asphalt pavement is greater than the



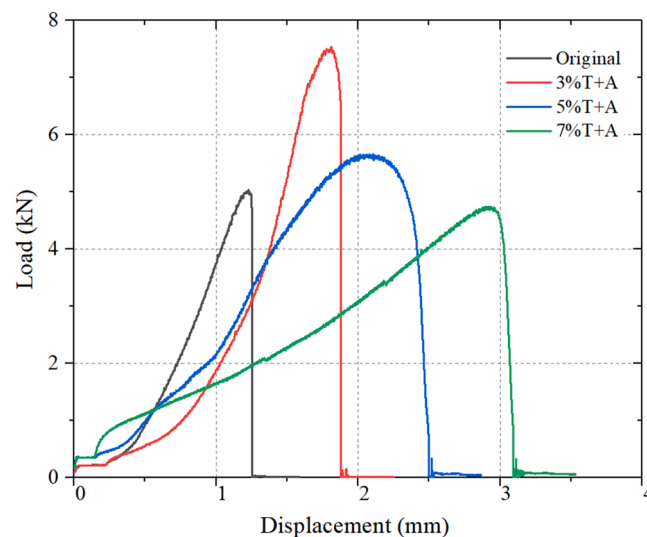


Fig. 13. Interlayer shear load displacement diagram.

**Table 14**  
Shear Strength between Coatings and Asphalt Layers.

No	Maximum load (kN)	Position corresponding to the maximum load (mm)	Interlayer shear strength (kPa)
Original	5.04	1.23	641.71
3%T + A	7.54	1.81	959.43
5%T + A	5.66	2.11	720.67
7%T + A	4.75	2.92	604.22

interlayer shear strength of asphalt concrete, and the interlayer rupture occurs mainly in the asphalt concrete part. The marking paint and asphalt pavement have good interlayer adhesion.

#### (2) Adhesion of cement pavement marking paint.

The interlaminar shear interface between cement concrete and paint is shown in Fig. 12, the test load displacement process is shown in Fig. 13, and the interlaminar shear strength is shown in Table 14. Cement in cement concrete binder is mainly cement, inorganic binder, do not have viscoelastic [37], surface coating set marking paint mainly rely on the adhesion of coating mucilage attached to the cement road surface. It can be seen from Fig. 12 that there is less white paint left on the cement concrete section of the original paint, and the interlaminar damage is shown by the peeling of the interface between the paint and cement; With the increase of toughening agent, the residual paint on the cement concrete base gradually increases, and the broken interface becomes the paint interface. It shows that with the increase of toughening agent, the adhesion between the modified coating and cement pavement increases gradually. It can be seen from Table 14 that with the addition of toughener, the viscosity-toughness of coating mucilage and the interlayer shear strength increase [40]. The interlaminar shear strength of 3%T + A is increased by 49.5% compared to the original coating. However, with the increase of toughener, the stiffness and strength of the coating decrease, and the interlayer shear strength of the coating and asphalt pavement decreases, but the interlayer displacement increases gradually. Because the excessive addition of the modifier can reduce the strength of the coating [18]. When the content of the toughening agent is not more than 5%, the interlayer shear strength is greater than that of the original coating, and is greater than that of the asphalt pavement. The results show that the toughening agent can improve the adhesion between the coating and cement pavement, but excessive modifier will reduce its strength, and the amount of toughening agent should not be more than 5%.

#### 3.3.4. Anti-aging performance

The anti-aging property of coatings was evaluated by ultraviolet aging test. The binder in the marking paint is mainly resin-based material. The ultraviolet aging process is similar to that of asphalt binder. The sensitive wavelength for ultraviolet aging is around 360 nm [24]. The ultraviolet spectrum is shown in Fig. 2b. At present, the generally accepted ultraviolet aging mechanisms of petroleum resin materials mainly include oxidation, physical hardening and volatilization of low-molecular-weight components [25]. Oxidation mechanism is the most significant mechanism during the ultraviolet aging process of asphalt. However, since the road traffic marking material has undergone the high-temperature construction process during service, thermal oxygen aging under service condition is no longer the main reason for the aging of road traffic marking material [43]. Physical hardening is a reversible process, which changes the macro technical characteristics of the marking paint, manifested as hardening embrittlement, but does not change its chemical composition [44]. Volatilization of volatile components (saturated and aromatic components), which is also considered to

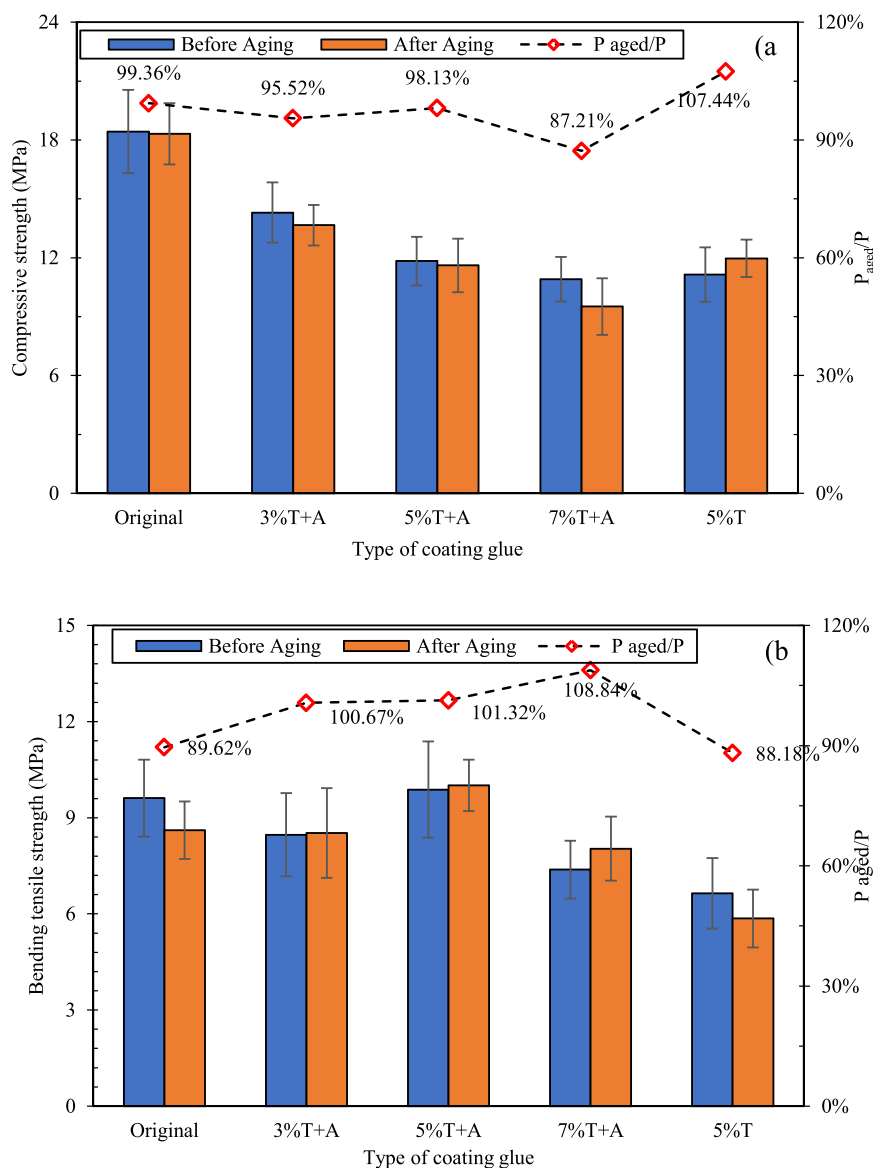


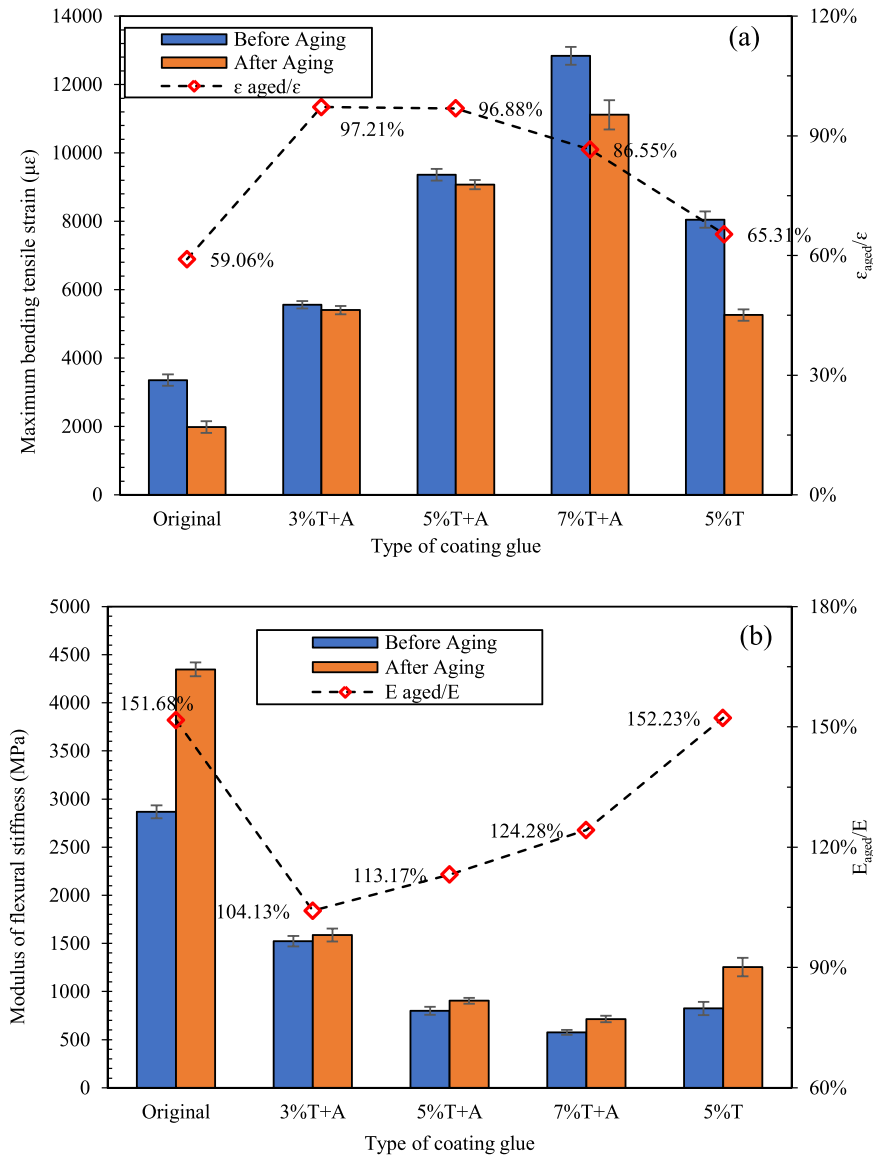
Fig. 14. Comparison of mechanical properties before and after aging (a: Compressive strength; b: Bending tensile strength).

be an aging mechanism, has little effect on the marking coating [29].

#### (1) Mechanical property.

UV aging test was used to evaluate the aging resistance of the coating. The comparison of mechanical properties of coatings before and after aging is shown in Fig. 14. It can be seen from Fig. 14 that the compressive strength of the original, 3% T + A and 5% T + A coatings have little change after aging. The compressive strength of 7% T + A coatings after aging decreases by 12.8%, while the compressive strength of the control group without anti-aging agent increases by 7.4% after aging. The modifier is high molecular polymer, which becomes hard and brittle after aging, and the modified coating loses viscoelasticity. Therefore, the compressive strength of 5% T coating in the control group without anti-aging agent increases slightly. Due to the high molecular compounds in the coating, aging is mainly physical aging, the initial aging will harden to increase its strength, and after aging, it will become brittle to reduce its strength [40]. The coatings without anti-aging agent exhibited severe aging. The material exhibits high brittleness and reduced strength, which are 10.38% and 11.82% lower than those of the original sample and the 5%T Bending tensile strength of the control group after aging. The addition of anti-aging agent can reduce the aging rate of the coating, and the aging degree is relatively low, manifested as a slight increase in strength [43]. In addition, with the increase of the content of toughener, the increase of Bending tensile strength becomes larger. The values of 3%T + A, 5%T + A and 7%T + A Bending tensile strength increase by 0.67%, 1.32% and 8.84% after aging.

#### (2) Low-temperature performance.



**Fig. 15.** Comparison of low temperature performance before and after aging (a: Maximum bending tensile strain; b: Modulus of flexural stiffness).

The comparison of maximum bending tensile strain and bending stiffness modulus of coatings before and after aging is shown in Fig. 15. It can be seen from Fig. 15 that the maximum bending tensile strain of the original sample and 5% T coating after aging decreased significantly by 40.9% and 34.7% respectively, while the maximum bending tensile strain of 3% T + A, 5% T + A and 7% T + A with anti-aging agent after aging only decreased by 2.8%, 3.1% and 13.5%. It can be seen from Fig. 15 that the bending stiffness modulus of the original sample and 5% T coating increased significantly after aging, increasing by 51.6% and 52.2% respectively, while the bending stiffness modulus of 3% T + A, 5% T + A and 7% T + A added with anti-aging agent only increased by 4.1%, 13.2% and 24.28% after aging. The anti-aging agent is an inorganic composite material, and the open micro-voids on the surface can partially absorb polar molecules capable of being oxidized, such as ketones, anhydrides, carboxylic acids and the like in asphalt, to prevent the polar molecules from being oxidized [24], the multi-layer layered structure can be uniformly distributed in the coating in a homogeneous mixed type, an intercalation type or a stripping type, and the required path is increased (a tortuous path) when ultraviolet radiation passes through the sheet structure, so that the penetration rate of ultraviolet radiation is reduced, and the anti-aging agent plays a protective role [14]. The anti-aging agent can shield most of the UV radiation and improve the anti-aging property of the marking, but the effect of improvement gradually decreases with the increase of the amount of toughening agent. When the content of toughening agent is 5%, the anti-aging property is better, and the anti-aging property is improved by about 40%.

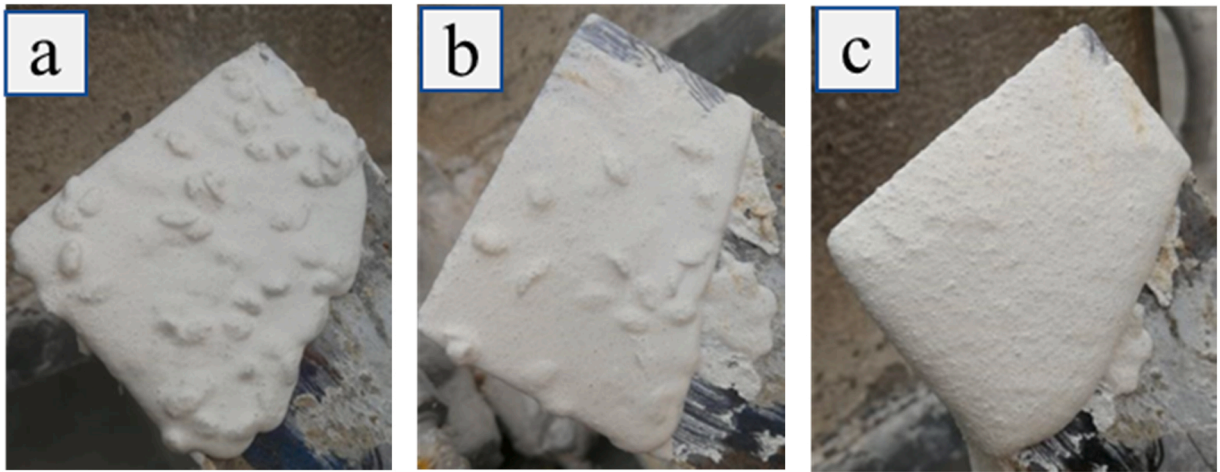


Fig. 16. Sampling appearance of mixed materials in high-speed mixing stage (a. 2 min, b. 5 min, c. 8 min).

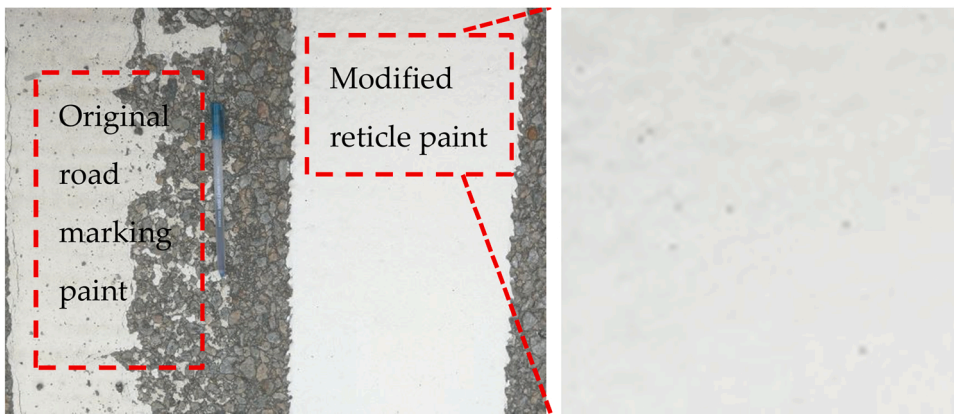


Fig. 17. Modified reticle appearance and details.

### 3.4. Study on working performance and construction quality

#### 3.4.1. Working performance

The construction of road marking paint is to use construction equipment by certain professional and technical personnel to apply different marking paints on the road according to the requirements of corresponding technical specifications [15]. The mixture mixing is divided into two stages: the first stage is unidirectional low-speed mixing in the feeding stage, which lasts for about 2 min, and the temperature range is 150 – 200 °C. The second stage is the forward and reverse alternating high-speed mixing stage after feeding, which lasts about 8 min and the temperature range is 200 – 240 °C. At the initial stage of mixing, there is obvious particle suspension on the surface, which gradually decreases in the middle stage, and at the later stage, the suspended particles completely disappear. The hot melt coating and mixed modified ingredients mutually soluble, has been mixing evenly [16], as shown in Fig. 16.

The marking process of the modified coating on the cement concrete base is relatively smooth, and the hot melt coating can flow out and be laid normally; The appearance and details of the marking are shown in Fig. 17. The appearance of the marking is uniform and complete, and the surface is free of wrinkles, spots; The film thickness is within the specified range, and the drying time is 1–1.5 min, meeting the requirements of specification  $\leq 3$  min; After curing, the marking surface shall be free of blistering, cracking, etc., and the glass bead shall sink normally, which has no obvious difference from the unmodified marking; The hardness of the modified marking has no obvious difference from that of the unmodified marking under mechanical engraving.

The modified coating can also be used for normal scribing on the asphalt base surface. The marking line shall be uniform and complete in appearance, and the surface shall be free of wrinkles, spots; The film thickness is within the specified range, and the drying time is about 1 min; After curing, the marking surface shall be free of blistering, cracking, etc., and the glass bead shall sink normally, which has no obvious difference from the unmodified marking; The hardness of the modified marking has no obvious difference from that of the unmodified marking under mechanical engraving.

According to the above process validation conclusion, the construction process of modified marking is consistent with that of

**Table 15**  
Sampling density.

Sample	Softening point of global method (°C)		Average (°C)
	1	2	
Sampling of the test section	109.65	108.24	108.95

**Table 16**  
Sampling parameters.

Number of sample	Cube (20 mm × 20 mm × 20 mm) test block						Average mass	Density (g/cm <sup>3</sup> )
	1	2	3	4	5	6		
Mass (g)	14.80	15.30	15.40	14.90	15.20	15.10	15.12	1.89

**Table 17**  
Sampling Low Temperature Bending Test Results.

No	Maximum breaking force (N)	Bending tensile strength (MPa)	Maximum bending tensile strain (μ <sub>e</sub> )	Modulus of flexural stiffness (MPa)
1	433.52	7.38	7954.17	927.22
2	339.31	5.77	9008.33	640.81
3	541.81	9.22	7283.33	1265.60
Average	438.21	7.46	8081.94	944.54

**Table 18**  
Compressive strength of sampling cube.

Test temperature (°C)	Specimen breaking pressure (kN)			Average pressure (kN)	Compressive strength (MPa)
	1	2	3		
23	5.83	6.12	5.81	5.92	14.80
50	2.96	2.42	2.34	2.57	6.43

conventional hot-melt marking paint [4], the indoor 5% T + A modified coating formula can meet the requirements of on-site construction.

#### 3.4.2. Performance of marking paint sampled on site

Softening point, bulk density, low temperature bending and compressive strength tests were carried out on the samples. Test results are shown in Table 15, Table 16, Table 17 and Table 18. The softening point and low temperature crack resistance test results of the sample are similar to the indoor test results, which are the expected test results. In the laboratory test, the 23 °C compressive strength of this group of modified markings was 11.83 MPa, slightly lower than the 12 MPa required by the specification. However, the 23 °C compressive strength of the test piece sampled on site was 14.80 MPa, which met the specification requirements. It may be that the on-site mixing process was better than the indoor mixing, and the mixing amount in the indoor test was less, which was not completely uniform [25].

According to the above test conclusions, the on-site sample tests have achieved the expected results [10], and the indoor basic formula can meet the specification requirements, with good durability.

## 4. Conclusion

A durable hot melt marker coating was designed and prepared by modifying the coating with toughener, rheological agent, and anti-aging agent to meet the requirements of high-quality marker coating in harsh environments and traffic. The main conclusions are as follows:

(1) Modified marker coatings have good basic properties such as fluidity, softening point, and drying time, but their compressive strength is slightly lower than that of original marker coatings. Compared with the original standard coatings, with the addition of toughener, the bending strain of the standard coatings tray increases by more than 60%, and the bending stiffness modulus decreases by more than 40%.

(2) Toughener greatly improves the adhesion between coating and asphalt pavement, and 5% toughener can increase the interlayer shear strength of coating and asphalt pavement by 53.38%. With the increase of toughener, the interlayer ring breakage interface of the coating gradually changes from the coating interface to asphalt mortar interface.

(3) The compressive strength of coatings has little change before and after aging. After aging, the maximum bending tensile strain

of coatings without anti-aging agent decreases by 34.7%, and the bending stiffness modulus increases by 52.2%, while after aging agent is added, the bending tensile strain decreases only 3.1% and the bending stiffness modulus increases only 13.2%.

(4) The field process validation has achieved the expected results, and the indoor basic formulation can meet the application requirements and has good durability. Modifiers can improve the properties of original coatings such as low temperature cracking resistance, adhesion, and UV aging resistance, and have a good application prospect in harsh environment areas.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

## Acknowledgements

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## Further reading

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