Study on non-destructive reinforcing material of modified one component polyurethane for tunnel crack disease prevention

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Abstract. In view of the defects of tunnel lining structure such as cracking and block dropping, cavity behind, honeycomb and pitted surface, construction joint dislocation and other defects, the technical research direction for non-destructive reinforcement materials in tunnel is proposed. The polyamide curing coating agent and one-component polyurethane protective material with high adhesion, good elongation, large tensile strength and rapid drying are developed. The above materials are described. The application technology and key points of brush coating, rolling coating and scraping coating can provide reference for related engineering application.

1. Introduction

China is the country with the longest railway operation mileage and the largest scale under construction in the world. By the end of 2019, the total length of China's railway operating tunnels is 18041 km, with a total of more than 16084[1]. According to the medium and long term railway network planning issued by the national development and Reform Commission, the railway operation mileage will reach 200000 km by 2030.

After the tunnel is in operation, the lining structure will have various defects or diseases due to unreasonable design, improper construction, geological disasters, operation years, climatic conditions and other reasons, mainly manifested as: lining cracking and block dropping, lining back cavity, honeycomb pitted surface, lining construction joint dislocation and other defects.

At present, the treatment measures for lining deterioration variation at home and abroad mainly include chiseling, caulking, cracking and grouting, all kinds of protective plates (NETs) and lining (arch), anchoring, local reconstruction, etc.[2-5]. For sections with serious diseases or insufficient lining thickness and strength, it is easy to cause secondary man-made damage in the process of reinforcement and treatment, which will damage the bearing capacity of the structure. The maintenance of force has a negative effect. In addition, for the existing operation lines, the above countermeasures and technologies are limited by the maintenance time. Therefore, the technical and economic problems involved are worth considering.

In recent years, non-destructive spray reinforcement technology has been widely used in the field of industrial and civil construction. By coating on the surface of concrete cracks and spalling areas, this kind of material can effectively strengthen the concrete in a certain range around the defects. This kind of technology concept is advanced and easy to implement, and has not been applied in the field of domestic railway engineering at present, and the related scientific research achievements are blank.
In this paper, a kind of high strength and high adhesion non-destructive reinforcement material for tunnel protection is proposed. Based on the demand analysis, the research and development technology and construction technology of the material are described in detail, which can provide some reference for engineering application.

2. Demand analysis

2.1. Types and manifestations of tunnel diseases
The forms of tunnel lining cracks are as follows: circumferential cracks, longitudinal cracks, oblique cracks, crescent shaped cracks, cross shaped cracks, etc.; the manifestations of lining block falling are: concrete pitted surface spalling, construction joint laitance falling block, etc. According to statistics, the crack disease of railway tunnel lining accounts for no less than 30%[3].

2.2. Construction characteristics of disease reinforcement project in tunnel
① The span of tunnel working face is large and the clearance area is large. The excavation span of single and double track tunnels of high-speed railway and single and double track tunnels of ordinary speed railway ranges from 6.98m to 13.30m, and the clearance is from 42.06 m2 to 100.00 m2. In strict compliance with the rules and regulations of railway tunnel construction, according to the characteristics of different tunnel span and tunnel operation space, select suitable and suitable rapid lifting equipment for operation, so as to improve the construction efficiency under the premise of ensuring safety.

② There are many facilities in the tunnel and the protection requirements are high. Tunnel equipment and facilities include catenary, contact suspension, support device, traction device, positioning pillar, communication and signal facilities, wall hanging cable and track rail, and most of the components are not allowed to touch.

③ Single day construction time is short. The construction process is greatly affected by the maintenance time of skylight, and the vault is located above the electrified catenary, which can only be carried out after power failure with the cooperation of power supply department, which is closely related to the process arrangement, construction process, equipment performance, personnel quality and the cooperation degree of property owners.

2.3. Material selection and coating form
According to the analysis of tunnel lining structure characteristics, hydrological information, disease types, causes and manifestations, it is determined that the materials should have high strength, high adhesion and convenient construction. The developed materials are the combination of non-destructive reinforcing materials and protective coatings, i.e. epoxy sealing primer, modified polyurethane with high strength and high adhesion for tunnel protection.

Among them, the epoxy sealing primer has excellent permeability to the concrete substrate, which can penetrate into the micro holes and cracks on the concrete surface, adhere to the lining concrete and solidify, and bond the defective concrete into an organic whole after forming. The single component material should reach high adhesion and strength after modification design. If it is coated on the solidified primer coating, the two layers should have good adhesion and good flexibility, and will not cause interlayer damage and shedding due to slight dislocation, expansion and other deformation of the lining.

3. Research and development of one component polyurethane protective material

3.1. Introduction of one component polyurethane materials
Polyurethane (PU) is a kind of polymer with carbamate group repeating unit on the polymer chain. In 1937, Otto Bayer, a German chemist, first discovered that polyurethane (formula 3-1) could be prepared by the reaction of isocyanate with alcohol compounds, and then it was applied in industry.
Since the 1960s, China began to independently develop and develop polyurethane resin. In recent decades, it has been developed rapidly, with a wide range of products, and has been applied in all walks of life.

Polyurethane materials are widely used in Railway Engineering, such as polyurethane curing track bed, polyurethane sleeper, polyurethane elastic ballast cushion, polyurethane Micro Foam elastic cushion, etc.; the above polyurethane materials are also widely used in high-speed railway vehicles for heat preservation, noise reduction, bonding, sealing, insulation and other purposes[6].

At present, polyurethane materials are mostly composed of two components. It is necessary to adjust the amount of isocyanate and the ratio of hydroxyl or other functional groups in the two components before use. It is necessary to adjust the later curing state by adding catalyst or other additives, and then carry out construction after mixing evenly. The two-component polyurethane has only a short service life after mixing, which needs to be adjusted according to the site temperature. The process is complex and can not meet the requirements of short skylight time.

Compared with two-component polyurethane, one-component polyurethane is more convenient to use and does not need to be prepared later. When used, it can be crosslinked and cured by heating or other methods, so the operation is more convenient. The later stage of one component polyurethane coating is moisture curing, mainly through the reaction of NCO in polyurethane prepolymer with moisture in the air (formula 3-2), so it has a long service life. After use, the remaining materials can be sealed and stored to prevent cross-linking and curing.

There are soft and hard segments in one component polyurethane. The main chain with good flexibility and polyol as soft segment, and isocyanate and chain extender as hard segment. Due to the thermodynamic incompatibility of hard and soft segments, the unique micro phase separation structure of polyurethane materials is caused. In addition to carbamate bond, polyurethane structure also contains ester bond, ether bond, urea bond, biuret bond, carbamate bond and acyl urea bond, which makes it easy to form hydrogen bond within and between molecules. There are many physical crosslinking points with strong binding force in linear polyurethane molecules. Therefore, it not only has the properties similar to amide groups, such as strength, wear resistance, oil resistance, but also has the heat resistance and solvent resistance of polyester, and the water resistance and flexibility of polyether.

In addition, isocyanate, the main raw material of polyurethane, is very active. It can not only combine with hydroxyl resin, but also with hydroxyl group in substrate to form strong chemical bond and hydrogen bond, which can enhance the adhesion with substrate.

3.2. Research on modification technology of one component polyurethane protective material
The common one component polyurethane protective material is easy to construct, but its strength is low after curing, the strength is 2 ~ 3Mpa, and the adhesion is poor. As a special material for tunnel protection, it should meet the characteristics of high strength, high adhesion, high elongation and fast surface drying speed, and should have good coating adaptability to ensure the coating quality and construction efficiency.
According to the above requirements, the material modification design was carried out

①To improve the adhesion performance, select the matching excellent epoxy sealing primer, improve the strengthening strength of concrete substrate, and enhance the interlayer adhesion with polyurethane topcoat.

②To improve the elongation and tensile strength, select suitable polyether diols, polyester diols and small molecular alcohols to synthesize prepolymers to meet the requirements of high elongation; increase the content of high cohesive groups, increase the chemical and physical crosslinking density, and increase the crystallinity to improve the strength of one component polyurethane materials.

③It is suggested that the surface drying time should be accelerated, and the non heavy metal catalyst should be selected to reduce the reaction activation energy and shorten the surface drying time.

④In order to meet the needs of spray coating, it is necessary to improve the sprayability, select the suitable solvent and reduce the viscosity of the system.

3.2.1. Epoxy sealing primer

After curing, the epoxy resin has good mechanical properties, high strength, strong adhesion (including with concrete substrate), small shrinkage, good electrical insulation, excellent chemical resistance, and good stability of the resin itself. Moreover, the epoxy resin has good leveling and permeability on the concrete substrate, which can seal the pores and cracks on the surface of the base material, and improve the surface strength of the base material to a certain extent. After curing, there are active functional groups on the surface of epoxy resin, which can participate in the reaction of other materials. For example - Oh can react with - NCO in polyurethane to improve the adhesion between the two materials. Bisphenol A epoxy resin is the most widely used epoxy resin. The curing reaction is generally ring opening cross-linking reaction between epoxy resin and amine curing agent (formula 3-3).

\[
\text{RCH-CH}_2 + \text{R}_1\text{NH}_2 \rightarrow \text{RCH-CH}_2\text{NCH}_2\text{CH}_2\text{OH}
\]

The curing strength and hardness of epoxy resin can be adjusted according to the epoxy equivalent and active hydrogen equivalent, and the compatibility of cured epoxy resin with polyurethane coating, such as interlayer adhesion and peel strength, should be met. High crosslinking density: the strength of epoxy resin is improved to a certain extent, but the wettability of polyurethane coating on the surface of epoxy resin becomes poor after too high, which makes the adhesion between layers and peel strength decrease. Low crosslinking density: the strength of epoxy resin decreases, so does the peeling strength. Therefore, it is necessary to select epoxy resin sealing primer with good compatibility, as shown in Table 1.

### Table 1. Performance of self-developed multi type epoxy primer and matching table with polyurethane topcoat

| General performance                  | Type I epoxy | Type II epoxy | Type III epoxy | Type IV epoxy |
|--------------------------------------|--------------|---------------|----------------|---------------|
| Surface drying time (h)              | <5           | <3            | <2             | <3            |
| Actual drying time (h)               | <24          | <24           | <8             | <24           |
| Adhesion of concrete substrate (MPa)| 5.1          | 5.1           | 5.2            | 5             |
| Adhesion with modified polyurethane (MPa) | 4.6         | 4.3           | 3              | ≥5 Substrate Failure |

RC H

\[
\text{RCH-CH}_2\text{OH} \rightarrow \text{RCH-CH}_2\text{NH}_2
\]
According to the characteristics of polyurethane materials, the matching performance of primer and topcoat when different curing agents are used in epoxy primer is verified. The verification results are shown in Table 2:

| General performance | Small molecular amine curing agent | Polyamide curing agent |
|---------------------|------------------------------------|------------------------|
| Surface drying time (h) | <2 | <3 |
| Actual drying time (h) | <8 | <24 |
| Adhesion of concrete substrate (MPa) | ≥5.2 | ≥5 |
| Adhesion with modified polyurethane (MPa) | 3 | ≥5 |

Comparison and analysis of the properties of the two kinds of curing agents:

Advantages of small molecular amine curing agent: high adhesion with concrete substrate, greater rigidity; fast curing of surface drying and solid drying; relatively low price. The disadvantages are: it is volatile and harmful to human body; after curing, the epoxy resin has high crosslinking density, low elongation and poor flexibility; the compatibility with flexible one-component polyurethane is poor, and the strength is only about 3MPa.

Advantages of polyamide curing agent: high adhesion with concrete substrate; high adhesion with modified polyurethane layer, good compatibility between the two, strength greater than 5MPa; low volatility of polyamide curing agent. The disadvantages are: compared with small molecular amine curing agent, the dry time is slightly longer; the price is higher.

According to the comparative analysis of the performance test data of the above two kinds of curing agents, the comprehensive performance of epoxy sealing primer is better than that of small molecular amine curing agent when using polyamide curing agent. It has good compatibility with polyurethane topcoat, high strength, good flexibility and elongation. Therefore, "polyamide curing agent" coating agent is selected.

3.2.2. One component polyurethane coating material

① By comparing polyether diols 1000, 2000, 3000 and polyester diols 1000, 2000, 3000, the strength of single component polyurethane prepared from polyester diols is higher than that of polyether diol polyurethane, and the low temperature flexibility of polyether is better. With the increase of molecular weight of polyether and polyester diol, the elongation increases, but the acid-base resistance of polyester diol is poor.

② With the increase of multifunctional alcohols, the crosslinking density increases and the strength increases after curing, but the elongation decreases more obviously.

③ One component polyurethane was prepared by Aromatic Isocyanates (MDI, TDI, crude MDI). Its strength is higher than that of aliphatic isocyanate (hmdi, IPDI) polyurethane. The strength of crude MDI is the highest, but the stability is poor. The viscosity of MDI is high, which is not conducive to spraying. The activity of aliphatic isocyanate is low and the adhesion with epoxy primer is poor.

④ The solvent containing carbonyl group can form hydrogen bond with carbamate group and has better solubility. Therefore, ester solvent and ketone solvent have better viscosity reduction effect than other non-polar solvents.

⑤ Polyurethane catalysts include metal catalysts (organotin, organic bismuth) and amine catalysts. In order to shorten the surface drying time, amine catalysts with obvious catalytic NCO and water reaction effect and metal catalysts with obvious catalytic NCO and - OH should be selected.

When the multi-functional raw materials and aromatic isocyanates are added, the crosslinking density of polyurethane topcoat is increased, and the high cohesive groups increase the strength of polyurethane coating, long-chain diols and polyols, and increase the elongation. Considering the later curing speed and elongation, the molecular weight of 2000-5000 diols and polyols were selected, and
a certain amount of organic bismuth and tertiary amine catalyst were added to accelerate the
crosslinking curing speed of polyurethane topcoat, so that the surface drying and real drying time were
guaranteed.

Table 3 shows the performance comparison of "modified single group polyurethane material",
"ordinary one component polyurethane waterproof material" and "two-component polyurea material". It can be seen that the "surface drying and real drying time" of modified single group polyurethane material is longer than that of polyurea material. A certain surface drying time also ensures that the material has enough wetting time on the concrete substrate, the crosslinking curing effect is guaranteed, and the reinforcement effect of lining concrete surface is improved.

**Table 3.** performance comparison of polyurethane protective coating, common polyurethane
waterproof coating and two-component polyurea

| Performance            | Modified polyurethane materials | Ordinary polyurethane waterproof | Two component polyurea materials |
|------------------------|----------------------------------|----------------------------------|----------------------------------|
| Smoke toxicity SR2     | —                                | —                                | —                                |
| Flammability classification S3 | —                                | —                                | —                                |
| Oxygen index 26.0%     | —                                | —                                | —                                |
| Tensile strength (MPa) | 33.7                             | 2-6                              | ≥16                              |
| Elongation at break (%)| 385                              | >300                             | >400                             |
| Breaking force (N)     | 230                              | —                                | —                                |
| Tear strength (N/m)    | 84                               | 35                               | ≥60                              |
| Acid resistance (5%)   | No visible change                | No visible change                | No visible change                |
| Alkali resistance (5%) | No significant change            | No visible change                | No significant change            |
| Neutral salt spray (NSS) | No significant change            | No visible change                | No significant change            |
| Water absorption (%)   | ≤5 (3.4%)                        | <5                               | ≤5                               |
| Adhesion (MPa)         | 5                                | >2                               | ≥2–2.5                           |
| Hardness (A)           | 15.90                            | Commonly                         | ≥90                              |
| Sanding abrasion (L/μm) | ≥1.42L/μm                        | No requirements                  | ≤0.50cm³/1.61km                   |
| VOC content (g/L)      | 158                              | <200                             | —                                |
| Proportion of solids (%)| >80                              | >80                              | >98                              |
| Liquid density (g/ml)  | 1.05                             | 1.05                             | 1.05–1.15                        |
| Viscosity (mPa·s)      | 14050                            | 8000–20000                       | 500–1500                         |
| Surface drying time (h) | ≤2                               | 6–12                             | ≤120S                            |
| Actual drying time (h) | 24                               | 24                               | ≤60s~10min                        |
4. Construction technology

4.1. Surface treatment of lining concrete

(1) Manual cleaning
Loose animals, oxide skin, sand and floating dust on the surface can be cleaned manually with shovel, steel brush, sandpaper and other tools.

(2) Power tool cleaning
Power tools can be used to clean the surface deterioration layer and local concrete with low bearing capacity. The commonly used power tools include power wire brush, impact tool, grinder and grinder.

(3) Water washing and cleaning
Clean water is used to wash the soluble substances on the concrete surface. If there are salt and other soluble substances on the surface of the lining structure, protection should be taken to prevent the soluble substances from being transferred to the adjacent base surface along with the water flow, resulting in the occurrence of new soluble matter pollution.

4.2. Coating conditions and methods

(1) Application conditions
Painting work should only be carried out in good atmospheric environment and weather conditions with appropriate temperature. It is not suitable for coating under the following conditions: ① when the temperature drops to the lower limit of the drying or curing temperature of the coating; ② there is open water on the surface of the lining concrete; ③ when the humidity in the tunnel is greater than 85%.

(2) Painting method
Brush coating: paint brush made of high-quality natural fiber or artificial wool, with appropriate size and matching paint.
Roller coating: according to the type of coating and surface roughness, choose the roller with suitable pile length. Generally, phenolic roller core is used, and drum sleeve with short or medium long velvet is used. The drum sleeve should be cleaned before use, and loose fibers should be removed.
Scraping and coating: the scraper is used for manual coating, and the scraper is made of metal or non-metal.
Spraying: spray the coating by spray gun with low pressure air flow of compressed air.
According to the actual situation of the tunnel, it is suggested that brush coating combined with scraping method should be preferred in construction. Although this method is slow in efficiency, it can effectively reduce the workload of field facilities protection and avoid paint mist pollution caused by spraying.

4.3. Key points of construction
The construction shall meet the following requirements:

(1) The amount of curing agent should be prepared in strict accordance with the requirements of epoxy sealing, and sufficient curing time should be ensured after mixing evenly.

(2) During the construction of epoxy sealing primer, the first coat should be thinned and repeatedly applied to prevent missing coating, so as to ensure the penetration and infiltration effect of epoxy sealing primer on the concrete surface, so as to make it fully penetrate and seal the pores and cracks on the concrete surface.

(3) When applying one component modified polyurethane topcoat, it is necessary to ensure that the surface of epoxy sealing primer coating is dry. Before application, the water absorbent towel can be used to wipe and then apply, which can effectively prevent foaming between the two coatings.

(4) In order to ensure that the normal operation of the line will not be affected during the construction of operating tunnel, the modified polyurethane topcoat should be given with enough surface drying time.
Due to the different regions of the tunnel, the process requirements are not the same. The specific construction technology should be in line with the actual situation of the tunnel location. According to the local climate environment, the internal characteristics of the tunnel and the window duration, the construction scheme with strong pertinence should be formulated to ensure the normal operation of the tunnel line and the smooth construction.

5. Conclusions
(1) Railway tunnel lining crack disease accounts for no less than 30%, concrete pitting and construction joint laitance falling off occur from time to time. By applying non-destructive protective materials on the concrete cracks and the outer surface of spalling area, strengthening the local concrete, preventing further crack development and falling block is the actual demand of current engineering maintenance.

(2) The developed polyamide curing coating has high adhesion to concrete substrate and high interlayer adhesion with modified polyurethane. The tensile strength between them is more than 5MPa, with low volatility and good applicability.

(3) The developed one-component polyurethane protective material has the characteristics of high adhesion, good elongation, large tensile strength and rapid surface drying, and has good coating adaptability, which can ensure the coating quality and construction efficiency.

(4) The developed polyamide curing coating agent and one component polyurethane protective material can be applied by brush coating, rolling coating, scraping coating and other processes, which is convenient for construction and is conducive to promotion.

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