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Development of shape memory polyurethane based sealant for concrete pavement

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HIGHLIGHTS

- SMPU based sealant with a tailored transition temperature is successfully prepared.
- Anti-aging property of SMPU based sealant is improved by added rutile TiO_2 particles.
- Prepared SMPU based sealant show satisfactory mechanical and shape memory properties.
- Developed sealant can better accommodate the working conditions of expansion joints.
- Suitable TiO_2 content is proposed to prepare SMPU based sealant for concrete pavement.

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ABSTRACT

Expansion joint failure is one of important causes to cause concrete pavement damages. To develop a new sealant to effectively seal expansion joint on concrete pavement, titanium dioxide/shape memory polyurethane (TiO_2/SMPU) composites with a tailored transition temperature (T_t) was prepared, and effects of TiO_2 content on various properties of TiO_2/SMPU composites were discussed. The results indicate that TiO_2 nanoparticles are uniformly physically filled in SMPU pores and wrapped by SMPU to form a compact skeleton structure when TiO_2 content is suitable. The tailored shape memory T_t of TiO_2/SMPU composites can be used as the shape memory switching temperature to match the working temperature of expansion joint in China. Also, TiO_2/SMPU composites include amorphous phases or microcrystal structures which are dominated by the presence of crystalline rutile TiO_2. The incorporation of TiO_2 leads to the decrease in crystallinity of TiO_2/SMPU composites. Additionally, a suitable content of TiO_2 can obviously increase the absorptivity of SMPU to UV light in the wavelength range from 300 nm to 400 nm, and also improve the reflectivity to visible light, lowering photo-aging properties of SMPU. Further, TiO_2 content shows a slight effect on shape fixity ratio of SMPU, but has an obvious influence on shape recovery ratio. Prepared TiO_2/SMPU composites show satisfactory shape memory property after a two-stage biaxial programming process. Finally, mechanical properties of SMPU are improved by a suitable TiO_2 content. The improvement in mechanical properties of TiO_2/SMPU composites can better accommodate the working conditions of sealant. TiO_2 content of 3% is proposed to prepare TiO_2/SMPU composites with a specially tailored shape memory T_t, which can meet engineering requirements of expansion joints when used as a sealant of concrete pavement.

1. Introduction

Sealant is widely used in building and traffic infrastructure [1]. For example, expansion joint is one of vital components on concrete pavement. These joints accommodate the movement of pavement slab caused by temperature changes, vehicle loads, humidity, shrinkage, creep, etc [2]. However, expansion joints are also weak links in a concrete pavement system. Expansion joint failure is a leading cause for structural damages of concrete pavement [2]. Studies on sealant were paid more and more attentions. Li et al. [3] reported a new adhesive strength test method to determine the adhesive strength of self-leveling and non-self-leveling silicone sealants, and proposed proper testing parameters. Liu et al. [4] prepared five asphalt based sealants modified by using different addi-

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tives, and found their properties were well related to the mixture performance of asphaltic plug joints.

Currently, hot-poured, cold-poured, or preformed sealants have been used to seal expansion joints on concrete pavement, but the existing sealants has shown adhesive failure, cohesive failure, and aging crack, leading to the increase in expansion joint failures and pavement damages [5]. Among them, polyurethane (PU) is one of important sealant materials due to such excellent properties as good toughness, abrasion resistance, easy preparation, and low price, etc [6]. Recently, a new PU material modified with hydroxyl terminated polydimethysiloxane was developed to use as a sealant of expansion joints on concrete pavement [7]. The sealant showed such better properties as tensile strength, cohesional strength, and fatigue resistance when compared with the conventional sealant. Carbonell-Blasco et al. [8] prepared the thermoplastic PUs to use as potential sealants which contained rosin or mixtures of rosin and 1, 4 butane diol in the chain extender.

However, these PU sealants have no shape memory performance, and it is difficult to better accommodate the working conditions of expansion joints on concrete pavement, leading to the decrease in their durability. It is known that PU can show shape memory properties when its components and synthesis are specially designed because PU has elastic network structures, including hard and soft phases [9]. The hard phase can form net-points that anchor the soft phase, keeping the original shape and playing a major role in the shape recovery process. The soft phase, on the other hand, maintains a temporary state after a programming process [9]. These are similar to other thermally induced shape memory polymers (SMPs). SMPs are usually composed of two components on the molecular level, including the cross-links to determine the permanent shape, and the switching segments with transition temperature (T_t) to fix the temporary shape [10]. According to the nature of switching segments, SMPs are further subdivided into two categories, including SMPs with amorphous switching segment where T_t is the glass transition temperature (T_g), and SMPs with crystalline switching segment, where T_t is the melting temperature (T_m) [10].

Among the above SMPs, the shape memory polyurethane (SMPU), as a kind of thermally induced SMP, was paid more attention because of its scientific and technological significance [11]. SMPU is block copolymer, including hard and soft segments. The soft phase is to maintain the temporary state of SMPU after deformation, and the hard phase is to maintain the original shape of SMPU [12]. SMPU often shows phase separation morphology due to the thermodynamic incompatibility between the two types of segments [12]. These block structure characteristics bring about obvious shape memory effects for SMPU. The content and arrangement of soft and hard segments in SMPU are different due to the variety of raw materials, molecular weight, etc. This causes SMPU to show different shape memory switching temperatures, which makes SMPU apply in various engineering fields [13].

Although SMPU has many advantages and was used in many engineering fields, it also shows such disadvantages as lower tensile and compressive strength, weaker thermal stability, smaller shape recovery force, etc [14]. However, these limitations can be improved by the reinforcing phases, mainly including fibers, particles, nanotube, graphene and so on [15]. In addition, it is known that polymer and its composites are easily subjected to photo-aging, and ultimately fail to meet performance requirements when exposed to heat, oxygen or ultraviolet (UV) light during its service life [16]. The anti-aging of polymeric materials in outdoor applications has become a crucial issue, and the most widely used methods were to add anti-aging additives in polymeric materials [17]. Researches on SMPU based composites have attracted more and more attention. Therefore, it is very necessary to select a suitable reinforcing phase which synchronously plays a role in improving mechanical and anti-aging properties of SMPU, prolonging its service life.

At present, such inorganic particles as TiO_2, Al_2O_3, silica, clay, etc. have become one of important approaches to reinforce SMPU based composites [18]. Among these particles, TiO_2 have recently received an increasing attention due to its non-toxic, tasteless, low cost, chemical stability, corrosion resistance and shielding to ultraviolet (UV) light [19]. It is known that TiO_2 exists in three major crystalline forms, including anatase, rutile and brookite, and the rutile TiO_2 is often used as UV blocker among the three kinds of crystalline forms [20]. Therefore, TiO_2, as a kind of environment-friendly filler, can play a role of both reinforcing phase and antioxidant, improving mechanical and anti-aging properties of SMPU [21].

Haghayegh et al. [22] synthesized SMPU based composites using clay nanoparticles as reinforcing phase, and found that the uniform dispersion of nanoparticles made the composites have good shape memory property. Li et al. [23] studied the effects of anatase and rutile TiO_2 nanoparticles on structures and properties of PU materials, and found that TiO_2 showed good UV protection ability and anti-fungal capacity. Thakur et al. [24] prepared a hyperbranched polyurethane–TiO_2/reduced graphene oxide composites with such properties as shape memory, self-healing and self-cleaning. Chen et al. [25] pointed out the interface interaction between nanoparticles and PU has crucial effects on microstructures and properties.

Further, SMPs and their composites must be experienced a programming or training process before they are endowed with shape memory effects. The main programming methods used for thermally induced SMPs are single-stage uniaxial or biaxial programming [26]. Among them, the single-stage uniaxial programming is widely used, but SMP materials are only endowed with the shape memory property in one direction. Although the single-stage biaxial programming is also utilized occasionally to endowed materials with the shape memory effects in two directions, the temperature control requirements of this method are complex, and the cost is high [26]. It is difficult to prepare sufficient quantities of programmed SMP materials for practical engineering applications.

Therefore, we made full use of advantages of the above two programming methods, and then a two-stage biaxial programming was developed to endow two dimensional shape memory effects to SMPU based sealant in the vertical direction at high temperature above T_t and in the horizontal direction at room temperature, respectively. It can improve the shape memory performance of SMPU based sealant, which can apply a consistent compressive stress to joint walls in the horizontal direction so that the adhesive failure can be avoided. Additionally, the prepared SMPU based sealant can prevent water from seeping into joints and also have self-healing capabilities so that the cohesive failure can be healed. Finally, this developed programming method can prepare enough sealants for meeting the demands of practical engineering applications.

However, it is noted that few studies have been conducted to reinforce SMPU with TiO_2 nanoparticles for using as a sealant of expansion joint, and fewer reports have been found to endow SMPU based composites with shape memory effect using two-stage biaxial programming method. Further, the high refractive index of TiO_2 makes it possible to become an alternative anti-aging additive [27]. The effects of TiO_2 on the photo-aging performance of SMPU based composites were seldom discussed although it was widely used in many engineering fields.

More importantly, a critical parameter for SMPU based sealant lies in its shape memory T_t. It is highly desirable to tailor the shape memory T_t of sealant according to its practical application environments. The reasons for this is only when the working temperature is close to the T_t of sealant, the premature shape recovery of sealant