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Preparation and characterization of microcapsule-containing self-healing asphalt

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ABSTRACT

Microcapsules-loaded with healing agent were successfully prepared in which dimethylphenol(DMP) or SBS/DMP forms core while urea/formaldehyde resin constitutes shell of the microcapsule. Microcapsule-containing asphalts displayed better mechanical properties than non-contained ones. The impact strength of microcapsule-containing asphalts improved over time. Microcapsule(DMP)-containing asphalt needed 7 days of rest time to restore its original strength, but it took only 3 days for microcapsule(SBS/DMP)-containing asphalt. This tells that microcapsule(DMP or SBS/DMP) containing asphalt posses excellent self-healing potential. SEM and X-ray photos illustrate that DMP on the asphalt fracture surface, which burst out of the microcapsules when cracks occur on the surface of the asphalt, undergoes polymerization to poly(phenylene oxide), filling cracks and healing damage.

Introduction

Generally asphalt cracks easily at temperatures around 20° C and around 60° C rutting(plastic deformation) occurs. Modifying asphalt means strengthening its physical properties in order to allow plastic deformation to occur at temperature higher than 60° C, and prevent asphalt from cracking too easily at low temperatures [1].

Although modified asphalt has greater durability compared to the straight asphalt, it still has limited lifespan. Minute cracks develop into potholes, disrupting comfortable driving, which is why necessity for self-healing asphalt has been the subject of research as it can retain sustained road surface for an extended period of time.

Self-healing material is a type of smart material that can heal damages resulting from use for a prolonged and return to its original form [2]. It originates from the fact that organisms heal themselves when they get injured. When a material cracks or is damaged, its physical properties change and can lead to breakdown of the material. Generally cracks can be repaired easily by hands, but minute cracks are usually too small to detect. If a material has the ability to repair small damages, it will reduce repair costs and production cost as well since the material will last longer, ultimately reducing CO_2 production.

Self-healing mechanism can be categorized into three classes: physical, thermal, and chemical mechanism. The physical mechanism can be subdivided into two types. In one type, nanopowder like montmorillonite are mixed with thermoplastic material [3–5]. When the material cracks or breaks, nanoparticles are getting close to each other since the medium is depleted and fill the cracks by crowding the empty space owing to polymer-induced depletion particle attraction [6]. In the other method, healing agent-contained microcapsules or glass tubes are mixed with the material [7–9]. This healing agent flows out when the material cracks and fills the empty space. Self-healing material using microcapsules is prepared by forming the microcapsule containing healing agent inside and by mixing them with matrix material. When material starts to crack, microcapsules on the crack propagation path are also destroyed, and healing material in the capsule leaks out filling the cracked hole. When the cracking of matrix occurred, monomer flows out from the microcapsules and is polymerized by the catalysts that exist in the cracked area. This polymer fills the crack area and repairs the matrix restoring its original form up to 80% on the basis of fracture strength. White [8] used dicyclopentadiene as healing agent and bis(tricyclohexylphosphine)benzylidine ruthenium dichloride(Grubbs catalyst) as catalyst. Using the ring-opening metathesis polymerization technique, White was able to self-heal the cracks in the thermoset material. Other self-healing materials using microcapsules were tested by Cho [9]. Here healing material was a mixture of polydimethylsiloxane

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and polydiethoxysiloxane with hydroxyl end group and the catalyst was di-*n*-butyltin dilaurate that healed microcracks on metal surface by condensation polymerization.

In the thermal mechanism, matrix contains compounds which use Diels–Alder reaction for polymerization or conductive materials such as carbon fiber and the matrix can be healed when heat is applied [10–12]. Furan molecules containing double bonds react upon heating (80° C) to give a network polymer, i.e., self-healing polymer, via Diels–Alder reaction [10]. More recently White [13] used a vascular (i.e., glass tubes) synthetic system to restore mechanical functions by shape reforming (i.e., filling up the crack) microcracks ($d > 35$ mm) with gelation within 20 min and by solidifying the gel through polymerization within 3 h.

In the chemical mechanism, cracks can be sealed by attraction of each side of the crack where the attraction force is one of the secondary valence forces (dipole interaction, hydrogen bond, ionic bond) [14–16]. Leibler [14] developed a self-healing rubber using supramolecule. Small molecules extracted from vegetable oil form 3-dimensional supramolecular structure by hydrogen bonding. In this case, hydrogen serves as an adhesive between atoms. When rubber is cut, unpaired hydrogen atoms are exposed at the intersection. If the cut surfaces are put back together, hydrogen bonds form again in 10 min and the material self-heals. After this healing process, the rubber maintains its original property that it stretches up to 4 times its original length. Even after being cut and reattached several times rubber maintains its characteristics as long as it is reattached within 12 h.

Asphalt is one of the most common types of pavement materials used in the world. It is a composite material that consists of a mixture of asphalt binder and aggregates. This material must resist all traffic loads in good conditions under many different climatic conditions for a long time. In order to maintain these characteristics during its lifetime, asphalt's wearing courses should be constantly maintained and repaired. Little cracking on a road can mean the start of large distress.

Recently, a number of researchers have demonstrated phenomenologically that asphalt mixtures have the capability to heal cracks [17–20]. They have shown that when given a certain amount of rest time, the modulus of asphalt mixtures can have some increase after the rest time and the overall life can be increased. These studies have led to a new way of describing the performance of asphalt materials: asphalts are healable.

As a complex composite material, asphalt mixture consists of two major components: asphalt binder and aggregates. Kim [19] and Song [21] proposed that in asphalt mixtures two types of healing exist: adhesive healing at the asphalt-aggregate interface due to the rebonding of the asphalt to the aggregates and cohesive healing within the viscoelastic asphalt binder due to the cross-linking of asphalt at the crack surface.

By far, three approaches to realize self-healing asphalt exist: the first one is that compounds are incorporated into asphalt binder to increase strength and repair bond. Lee [22] and Pang [23] found that SBS positively affect the self-healing of asphalt. Little [31] explored the possibile effect of hydrated lime on healing ability of asphalt. Hydrated lime—added asphalt when it has a high asphaltene content showed healing ability. The second one is that embedded encapsulated chemicals are used in asphalt binder to decrease stiffness and repair bond. Microcapsules filled with maltene are mixed with asphalt mixture [24]. When a crack appears in the pavement close to a microcapsule, it would be broken and the maltenes will be in contact with the asphalt around. It will rejuvenate the asphalt and enhance self-healing. In another study [25], embedded microcapsules containing rejuvenator were prepared, and healing capability was validated with tests. The third one is that local heating inside the asphalt with induction energy is used to repair the binder and to improve the properties again [26,27]. Steel wool was added to asphalt mixtures. The steel wool heated by induction energy melts the asphalt that flows into the microcrack and fixes the aggregates back to pavement surface. Thus the system reduces raveling. A problem of this system is that it requires human intervention to complete the healing process.

It is proposed that the healing of asphalt is a three step process [28,29]: (1) wetting of the faces of a crack, (2) diffusion, caused by Brownian motion, driving the molecules to the low-energy region near the crack, and (3) randomization of the diffused molecules to attempt to reach the original strength of the material.

Polyphenylene oxide(PPO), one of the engineering plastics, can be manufactured by polymerization of 2,6-dimethylphenol(DMP) through oxidation reaction of oxygen molecules using cuprous chloride as the main catalyst and pyridine or di-*t*-butylethylenediamine as cocatalyst [30]. DMP also self polymerizes into PPO in asphalt by the components of asphalt, vanadiums and amine compound [31].

In this study, monomer DMP and SBS(styrene–butadiene–styrene triblock copolymer) rubber were used as healing agent. They were used as core material in producing microcapsules and incorporated into manufacturing self-healing asphalt. It was hypothesized that DMP will polymerize into PPO by metals in asphalt and by oxygen molecules in the air and this will seal the crack and consequently heal the material.

Experimental

Materials

Urea and formaldehyde to prepare urea(U)/formaldehyde(F) resin, which forms the shell of microcapsules, were purchased from Samchun Chemical. 2.6-DMP and SBS(KTR101, linear type), which constitutes the core of the microcapsules, were obtained from Aldrich and Kumho Petrochemical, respectively. Triethylenetetramine(TETA) which can liquify DMP and SBS to be used as core solution of the microcapsule was purchased from Aldrich. Polyvinylalcohol(PVA) and sodium dodecyl sulfate(SDS) which were used as emulsifier and surfactant each for preparing emulsions purchased from OCI and Aldrich, respectively. Asphalt(AP-5, penetration 60–70) was provided by SK Petrochem.

Preparation of microcapsules

For preparing the microcapsule, emulsion was first made that in 1000 ml reactor distilled water 200 ml, emulsifier PVA 2.2 g and surfactant sodium dodecyl sulfate 0.5 g were added and thoroughly mixed. Prepolymer forming the shell of the microcapsule was made that urea 3.6 g reacted with formaldehtde 0.9 g at 70° C for 1 h in another container. TETA 2 g was used to liquify DMP 5 g for DMP only forming the core. Thus DMP solution for the core was obtained. For SBS and DMP both forming the core, TETA 2 g dissolved DMP 2.5 g first and then SBS 2.5 g. Thus SBS/DMP solution for the core was obtained.

Reactor containing the emulsion was set up in a bath and the core solution(DMP or SBS/DMP) was added and mixed at 70° C for 30 min. Then the prepolymer was added and stirred at 250 rpm and reacted for 3 h while adjusting pH to 3. The emulsion solution was washed and filtered using water containing 10% methanol then separated microcapsules were dried in a vacuum oven at 30° C for 5 h.

Yield (Y_{mc}) of obtaining the microcapsule was calculated using the following equation;

$$Y_{\mathrm{mc}} = \left(\frac{W_{\mathrm{mc}}}{W_t}\right) \times 100$$

where W_{mc} is the weight of obtained microcapsule and W_t is the weight of all agent composing shell and core of the microcapsule.