STUDY OF SILICA GEL AS SELF-HEALING AGENT IN ORDINARY PORTLAND CEMENT (OPC) MORTAR EXPOSED TO EXTREMELY HIGH TEMPERATURES

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ABSTRACT

The study was conducted to investigate the effect of silica gel on the behaviour of Ordinary Portland Cement (OPC) mortar as self-healing material after exposed to extremely high temperature. An attempt has been made to define whether the spherical silica gel can carry out the healing mechanisms after put into the furnace and burn under extremely high temperature (500˚C, 600˚C and 700˚C). Three same dosages of silica gel (1% by weight of OPC) in the mortar mix were applied. There were other three sets of mortar mix without silica gel that were prepared to act as control specimen. Mortar properties after 3 days, 28 days, and exposure to extremely high temperature were conducted to study the compressive strength and its porosity. In order to determine its mechanical properties, 45 cubes (50 mm) with silica gel and another 45 cubes (50 mm) without silica gel were cast. All cubes specimens were tested until failure in compression machine. Based on the experimental results, silica gel will start to be activated after reacted with water (for day 3), which had almost similar strength with control cubes. However, in elevated temperature exposure, the compressive strength of cubes with silica gel is not influenced by the silica gel contribution once the temperature was elevated beyond 500 ˚C. The expansion of silica gel was believed to lead to the crack occurrence and decreased the strength of mortar cube. The percentage of porosity for OPC mortar with silica gel are much higher than the control cubes, means that it is more permeable than those control cubes due to the expansion development of the silica gel as the crack observed on mortar’s surface was happened at the interfacial transition zone between silica gel and cement matrix. Conclusively, the results revealed that silica gel only give significant effect to the compressive strength at day 3 and at 500˚C heating temperature.

ABSTRAK

Kajian eksperimen yang dibuat bertujuan untuk mengkaji sama ada gel silica yang memberi kesan kepada mortar Portland simen biasa ketika digunakan sebagai sebagai bahan penyembuhan diri selepas terdedah kepada suhu yang sangat tinggi. Percubaan telah dibuat untuk menentukan sama ada gel silika sfera boleh melaksanakan mekanisme penyembuhan selepas dimasukkan ke dalam relau dan membakar di bawah suhu yang sangat tinggi (500C, 600C dan 700˚C). Tiga dos yang sama jenis gel silika (1% mengikut berat OPC) dalam campuran mortar telah digunakan. Terdapat tiga lagi set campuran mortar tanpa gel silika yang bersedia untuk bertindak sebagai set spesimen kawalan. Sifat mortar selepas 3 hari, 28 hari, dan pendedahan kepada suhu yang sangat tinggi telah dijalankan untuk mengkaji kekuatan mampatan dan keliangan. Dalam usaha untuk menentukan sifat-sifat mekanikal, 45 kiub (50 mm) dengan gel silika dan 45 kiub (50 mm) lagi tanpa gel silika dibaringkan. Semua kiub spesimen telah ditimbang dan diuji sehingga gagal dalam mesin mampatan. Berdasarkan keputusan eksperimen, gel silika akan mula diaktifkan selepas bertindak balas dengan air (untuk 3 hari), yang mempunyai kekuatan hampir sama dengan kiub kawalan. Walau bagaimanapun, dalam pendedahan suhu yang tinggi, kekuatan mampatan kiub dengan gel silika tidak dipengaruhi oleh sumbangan gel silika selepas suhu telah dinaikkan melebihi 500 C. Pengembangan gel silika dipercayai menyebabkan berlakunya retak dan menurun kekuatan mortar kiub. Peratusan keliangan bagi OPC mortar dengan gel silika adalah jauh lebih tinggi daripada kiub kawalan, bermakna bahawa ia adalah lebih telap daripada yang kiub kawalan akibat kriteria pengembangan gel silika sebagai punca retak kerana ia diperhatikan pada permukaan mortar pada peralihan antara muka zon antara gel silika dan matriks simen. Muktamad, keputusan menunjukkan bahawa gel silika hanya memberi kesan yang ketara kepada kekuatan mampatan pada hari 3 dan pada suhu 500˚C pemanasan.

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LIST OF SYMBOLS

MPa	Mega Pascal
mm	Millimetre
˚C	Degree Celsius
μm	Micrometre

LIST OF ABBREVIATIONS

OPC	Ordinary Portland Cement
SHA	Self-Healing Agent
$Ca(OH)_2$	Calcium Hydroxide
SAP	Super Absorbent Polymers
ECC	Engineered Cementitious Composite
PE	Polyethylene
PVA	Poly Vinyl Alcohol
SC	Steel Cord
PP	Polypropylene
$CaCO_3$	Calcium Carbonate
PMC	Polymer Modified Concrete
EVA	Ethylene Vinyl Acetate
CO_2	Carbon Dioxide
MMA	Methyl Methacrylate
CA	Cyanoacrylate
$CaC_6H_{10}O_6$	Calcium Lactate
Na_2SiO_3	Sodium Silicate
C-S-H	Calcium Silicate Hydrate
UFF	Urea Formaldehyde Formalin
TEB	Triethylborane
SEM	Scanning Electron Microscopy
SiO_2	Silica Oxide

CHAPTER 1

INTRODUCTION

1. 1 Introduction

Concrete is one of the materials which used widely around the world for various structural purposes because of its characteristics of fire resistant, low maintenance, cost affordability, high compressive strength and durability, etc. However, concrete is susceptible to concrete as a bottom line of its low tensile characteristic. To overcome this problem, it can be installed reinforcement bar inside concrete to hold the tensile load and able to restrict crack width which supposed to be hold by concrete that sensitive to crack formation. Although concrete with reinforcement bar able to restrain tensile load, but still not perfect enough to prevent the crack formation.

The width of the crack will jeopardize the durability of structural as the concrete was exposed to the attack or penetrated into matrix along the crack by liquid or gases and cause damage to the concrete. Because of the existence of aggressive liquid and gases, the crack might grow wider lead to the exposure of the reinforcement to air surrounding. The total collapse of the structural might be happen after the reinforcement start to corrode. Thus, it can be seen that the process of maintenance and repair of concrete crack is significant to maintain the durability of the concrete.

However, the crack repair process is complicated and hard since the concrete is hard to be seen and reached. In addition to the budget and cost for repair concrete is high and the result is unpredictable. Therefore, the Self-Healing of cracked concrete will be more effective and cheaper if compared with crack repair.

Self-healing technique was mentioned as the ability of a crack in cementitious materials to seal them by own. Jaroenratanapirom & Sahamitmongkol (2011) found that there are two categories of self-healing mechanism which are small capsuled with adhesive material and limit amount of hydrates that remained inside the concrete to heal the crack. Meanwhile, Tittelboom & Belie (2013) stated that there are three groups of self-healing in cementitious materials which are intrinsic healing; vascular healing and capsule based healing. In 1969, a research conducted by Malinskii et al. were the first time concept of self-healing mechanism manipulated and built inside the polymeric materials.

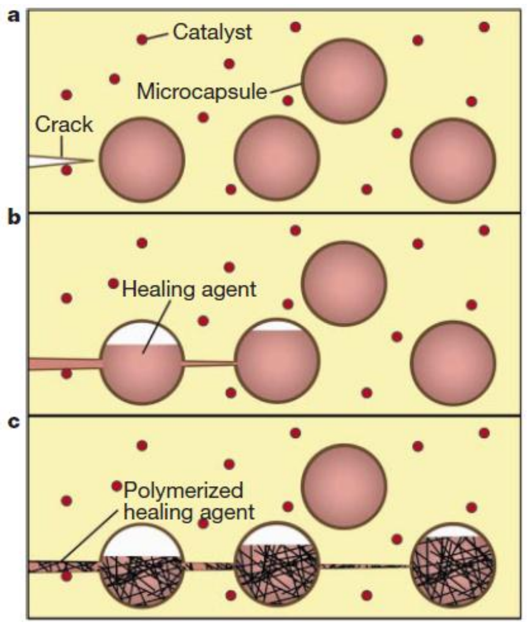

Figure 1.1: The autonomic healing concept. a, Cracks form in the matrix; b, the crack ruptures the microcapsules, releasing the healing agent into the crack; c, the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed

Source: S. R. White et al. (1982)

The research (Wool, 1979, 1981) specified that the crack self-healing in thermoplastic and cross-linked system were come into the sight. Its effect on the mechanical behaviour of some semi crystalline polymer, block copolymer and field elastomer was explored as a function of time, temperature and strain. White et al. (2001) investigated that structural polymeric material with the ability to heal itself automatically.

1. 2 Problem Statement

Concrete is the most widely used man-building material for structural construction. However, the particularly cracking of the concrete cover layer which lead to the reducing durability as water penetration and other chemical attacks toward the concrete along the crack width.

Concrete crack might occur at any phases of concrete life cycle. It can be due to the problem of concrete itself, poor quality of material or external factors such as support loading overload, critical environment exposure, critical temperature, poor workman ship and design deficiency.

Concrete element will start decompose after exposed to high temperature that beyond its maximum limit. Limited works have been carried out to examine the actual optimum temperature that can be sustained by concrete under high temperature. Hence, different temperature shall be exposed by concrete to find out its optimum temperature before crack. There are different arguments about properties of concrete exposed to less than 300˚C; the compressive strength definitely decreases when the heating temperature is above 300 ˚C. Sancak et al. (2008) stated that decreases beyond 100 ˚C from a peak at 100 ˚C. The other studies that mentioned dramatically reduction of compressive strength of about 40% as occurs about 500˚C - 600˚C (Ichise et al. 2001). Balogun (1986) investigated the concrete’s compressive strength at 600˚C would be deducted up to 50 %. At 800 ˚C, Sancak et al. (2008) examined there is a reduction of strength from range 74% to 97% of normal concrete.

There were massive amount of money spent by neither government nor society due to lack of durability of concrete structure. The cost for demolish and reconstruction of building is high; as discussed by Cailleux and Pollet (2009), the cost consist of repair works amount to half of the annual construction budget. Thus, more researches about self-healing in cementitious material mechanism shall be studied and investigated in order to reduce the cost for repair concrete in the market nowadays.

Plenty research has been conducted previously are focused on effect of the strength grade of concrete where exposed to high temperature (Balagun 1986; Ichise et al. 2001). Ichise et al. discussed the criteria of different kinds of high-strength concretes under high temperature. However, there is limited research on the behaviours of capsule based self-healing after exposed to the high temperature. The different types of self-healing materials such as silica gel can be include to identify whether the excessive water will react with the additional silica oxide, SiO_2 which provided by silica gel. This will results in conclusions and recommendations to help minimize the amount of budget that going to spend every year for building maintenances purpose by using silica gel.

1. 3 Research Objectives

The main objective of this research is to determine the suitability of Silica Gel as Self-Healing agents in OPC after exposed to extremely high temperature (500˚C, 600˚C and 700˚C respectively).

While the sub-objectives of this research are:

1. To determine the strength and porosity of Ordinary Portland Cement mortar after exposed to extremely high temperature
2. To identify the effective extreme high temperature exposure for Silica Gel as a Self-Healing agents

1. 4 Scopes Of Research

There are several scopes of research have to consider to make sure that the research can proceed based on the schedule and planning. The concrete mix design compressive strength for the mortar cubes is 30MPa at 28days. For cube test, there are total 90 mortar cubes (45 mortar cubes with silica gel and vice versa) are moulded in 50 x 50 x 50 mm which will be tested for its strength and porosity at age 3 and 28 days. For compressive strength test and water porosity test, there will be 15 control mortar cubes (with silica gel) and 15 mortar cubes (without silica gel) are moulded in 50 x 50 x 50 mm will be tested in compression machine at age 3 and 28 days for each different temperature. Three mortar cubes will undergo compressive test at day 3; three mortar cubes will undergo compressive test at days 28; three mortar cubes will undergo compressive test at days 28 which exposure to extremely high temperature; whereas another 6 mortar cubes will undergo porosity test to test its density, percentage of absorption and present voids in hardened mortar cube. Three different temperatures are set before put into furnace, namely: 500˚C, 600˚C and 700˚C and maintain the temperature for duration 30 minutes after reach target temperature (high temperature exposure was conducted on 28 days specimen only). All results get at day 3 and day 28 will plot in graph and compared with geopolymer concrete. Superplasticizer is added to increase the workability and mobilizing of mortar during mixing.

1. 5 Significance Of Research

The research of self-healing in Ordinary Portland cement after exposed to high temperature is significant because it investigates how far the temperature of Ordinary Portland cement‘s mortar can be sustained before it start to crack after the exposure of extreme high temperature. Moreover, the research is also determining the optimum temperature for Self-Healing agent, silica gel to operate well before the self-healing agents start to malfunction. Durability of the concrete is always concerned by engineers in the material design. This is generally accomplished by providing proper mix design proportion. In order to resolve the issues involving formation crack of concrete, additional proportions of self-healing spherical capsule, silica gel has to be added in by referring the amount of 1 % of Ordinary Portland cement, which will be consumed itself to take out their own duties . In this respect, two self-healing mechanism will be carry out: unhydrated cement particles on going hydration process; the second self-healing mechanism is triggered through the consumption of agents after breakdown of capsule layer and healing process occurred in region of damage. Furthermore, the special interest of the present research is to determine the incident factors when the Ordinary Portland Cement mixture crack and silica gel will activate as well after heat up to extremely high temperature and how its efficiency is. The mortar with silica gel after exposed to high temperature will crack and the silica gel will start to activate in simultaneous to heal back the crack to minimise the loss of durability.

1. 6 Overview Of Research

Chapter one introduced the background of the concrete, crack formation and crack healing mechanism. In this chapter also showed the problem that might be faced in the construction site nowadays. There are also other subtopic such as research objectives if the research, scope of the research, significance of research and expected outcome that can get after conduct the research.

Chapter two is the literature review that listing all the research, studies of journals and articles that done by the authors. Firstly, there are three groups of the self-healing mechanism are going to discuss in this chapter. Subsequently, the different types of healing agents, suitable encapsulation technique, techniques used to evaluate self-healing efficiency, and comparison with previous studies are also considered and discuss in these chapter.

Chapter three will discuss the research methodology that will be using to conduct the experiment and research. The preparation of materials used for conduct the research, procedures of the sample specimens, flow chart of the experiment and the justification of the research.

Chapter four will analysis the data and results after conduct the experiment such as porosity test and compressive strength test. The graph of compressive strength and permeability of mortar cube will be plotted and the result will be discuss and compared for the concrete with silica gel and without silica gel.

Chapter five is the conclusion and recommendation, the recommendation to improve the research after analysis the result that has done in previous chapter. The conclusion also considered in the last chapter, which mentioned whether the silica gel is suitable and effective as the self-healing materials.

CHAPTER 2

LITERATURE REVIEW

2. 1 Introduction

The purpose of this chapter is to provide a review of past research efforts related to self-healing mechanisms, selection of SHA, suitable encapsulation technique and suitable technique to evaluate healing efficiencies. There were also other relevant research studies listed to compare their advantages and disadvantages.

2. 2 Self-Healing Mechanisms

Self- Healing is an old and well known technique for construction part as it takes places where some natural healing properties occurred in concrete. It was actually occurred naturally due to continuously of hydration process that take placed in concrete or carbonation of Calcium Hydroxide ($Ca(OH)_2$); the crack may heal in slow rate. Although it acquires healing ability but only limited to small cracks and its healing region is unpredictable and not under control for the area extended to be healed by the agents. Sum more the hydration process only can take place when there is availability of water around the concrete. In spite of this slow rate of natural healing properties, the concrete can be adjusted to another types, which is built in with autogenously crack healing.

Malinskii et al. (1969) were the first team to publish the self-healing properties which embedded inside the poly. Malinskii et al. investigated the self-healing of cracks in polymers by determine the effect of the molecular weight of a polymer and the environment on self-healing of cracks in polyvinyl acetate. It was confirmed that any change of the relaxation spectrum of the polymer affects the self-healing process occurring at the crack tip. Meanwhile, Dry (1994b) was the first who proposed the intentional introduction of self-healing properties in concrete.

Furthermore, there are also further investigations carried out by Malinskii et al. (1970) to study the effect of the medium and the thickness of the polymer film on the self-healing of cracks in polyvinyl acetate. Malinskii et al. claimed that the "recovery" coefficient decreases when healing takes place in the presence of the vapour of a surface-active agent and increases under conditions such that water molecules are desorbed from the surfaces of the crack where transition occurred from a thick to a thin layer of polymer slows down the rate of the self-healing process.

Wool (1979) claimed that the self-healing agents also have the effect on the mechanical behaviour of some semi crystalline polymers, block copolymers and filled elastomers. It was found that cracks or micro voids could heal instantaneously or slowly depending on the microstructural damage and molecular rearrangements incurred during the de-bonding process. Crack healing rates increased with temperature and no healing was observed below the effective of the active molecular healing components in each material.

Wool and Connor (1981) investigated the theory of crack healing in polymers is presented in terms of the stages of crack healing which included surface rearrangement, surface approach, wetting, diffusion, and randomization. The recovery ratio of mechanical properties with time was determined and the applications of the theory are described, including crack healing in amorphous polymers and melt processing of polymer resins by injection or compression moulding. Besides that, chain fracture, creep, and stress relaxation are also discussed. New concepts for strength predictions are introduced.

Dry (1994a & 1996a) has investigated concrete and cement permeability (due to cracking and porosity) and found that brittleness can be addressed by the incorporation of chemicals in fibres, which are later released. The main objective of the research was specifically concerns the repair or healing of cracks and filling of voids in cementitious matrix by the internal release of repair chemicals from inside fibres into the hardened matrix. Dry then continue the investigation of the healing of cracks on polymers.

White et al. (2001) was studied that structural polymeric material with the ability to automatically heal the cracks. The material incorporates a microencapsulated healing agent that is released upon crack intrusion. Polymerization of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces. Figure below further illustrates the rupture process of an embedded microcapsule.

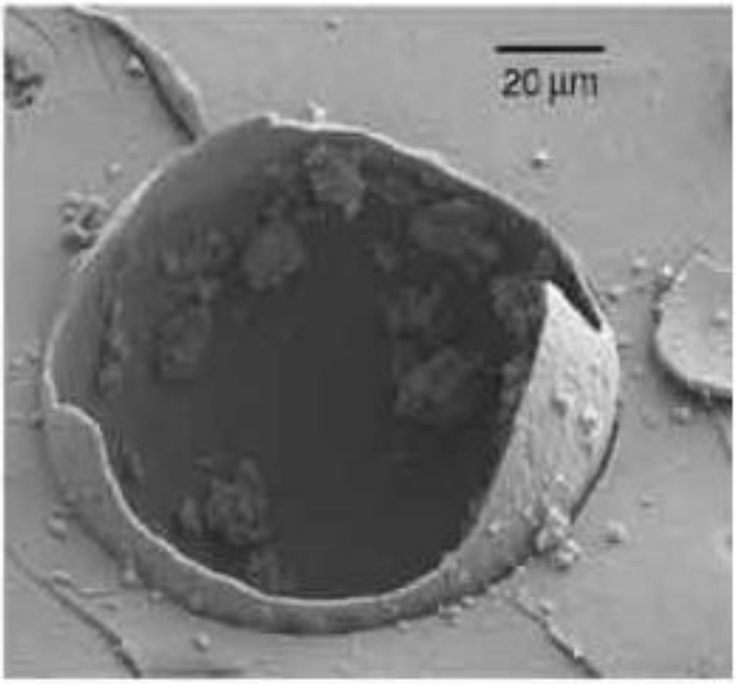

Figure 2.1: A scanning electron microscope (SEM) image shows the fracture plane of a self-healing material with a ruptured urea formaldehyde microcapsule

Source: White et al. (2001)

Self-healing in cementitious materials can be divided into three groups like what Kim & Nele (2013) stated before, which are: Intrinsic healing, vascular healing and capsule based healing. Every healing mechanism listed above also used to provide last defensive protection by heal the crack and damaged region.

2.2.1 Intrinsic Healing

Intrinsic self-healing materials do not have a sequestered healing agent but instead have a latent self-healing functionality that is triggered by damage or by an outside stimulus. It might be happened due to the composition of the cementitious material itself. The intrinsic healing mostly contributed by the autogenous healing, improved autogenous healing or reaction of polymeric substances.

2.2.1.1 Autogenous Healing

One of the most common and widely studied mechanisms of intrinsic crack healing is autogenous healing. The autogeneous crack healing are classified into two mechanisms: excessive amount of cement particles that haven't take place hydration process inside concrete and existence of Calcium Hydroxide ($Ca(OH)_2$). Both of the mechanisms above also have a same problem, autogenously healing are depend on the concrete age at time of cracking. Neville (2002) claimed that, further hydration of anhydrate cementations components is mainly due to the natural self-healing properties in concrete. However, this process only applies to very young concrete and the formation of calcium carbonate most likely causes self-healing at later ages. Natural self-healing can be useful for cracks with widths up to 0.1–0.2mm.

There were many study related to the maximum crack width that can be healed by autogenous healing made by various authors. N. ter Heide et al. (2005, 2006 & 2007) investigated that narrower width can be completely healed by this type of healing mechanism.

2.2.1.2 Improved Autogenous Healing

The improved autogenously healing is another improvement mechanisms that enhance the self-healing coverage to the crack in concrete. The appropriate amount of water supplied towards the concrete might promote the previous healing action and also improve the hydration and crystallization process inside the concrete.

There were authors investigated the possibility to mix super absorbent polymers (SAP), which also known as hydrogel to provide sufficient water to stimulate the healing process during dry condition around concrete in simultaneously provide direct blocking effect by expanding beyond the pore (Lopez-tendero et al., 2011). The SAP are cross- linked polymer that able to absorb up to certain amount liquid and swell to form a soft and insoluble gel which very sensitive on the pH value concentration of the solution embedded. As the initial swelling will lead to the formation of pore exist inside concrete after placing of concrete and hardened which will affect the strength gained, Lopez-tendero et al. tried to modify and improve the criteria of the SAP to prevent swelling at alkaline state.

Besides that, there were some researchers proposed to heal the concrete by using the fibre reinforced strain hardening engineered cementitious composite (ECC) to restrict the crack width as mechanism to heal the concrete. Li et al. (1998) were used polyethylene (PE) fibres and continue with Poly Vinyl Alcohol (PVA) fibres which resulted the maximum crack width remain below 60µm. Homma et al. (2009) and Nishiwaki et al. (2012a) were compare the efficiencies of different fibres such as steel cord (SC), Polypropylene (PP), PE and PVA fibres and claimed that PVA fibres induced the highest healing efficiency. Nishiwaki et al. (2012b) further their studies by combine the PVA fibres with embedded brittle tubes containing healing agents. Nishiwaki et al. concluded that healing was more efficient when cracks became larger than 200µm; the PVA fibres were not enough pulled out below 200µm.

Other attempts to stimulate autogenous healing are addition of agents which will form crystals inside the crack. Most of the researches done previously were replace certain percentage of the cement by pozzolanic materials and latent hydraulic materials

when the hydration process and pozzolanic reaction continue ongoing since there was excessive amount of binders remain unhydrated. Sisomphon & Copuroglu (2011) add up other expansive additives to form ettringite crystal to fill the crack. However, the continuous expansive reaction like sulphate attack was lead to the micro-cracks between matrixes and aggregates. Jonkers (2007) suggested to use $CaCO_3$ precipitating bacterial spores as the healing agents. However, both of mechanisms also have the disadvantages and side effects. For addition of expansive additives, the agents will be finished since the amount of agents inside concrete is limited but the continuously hydrate or crystalize action will be proceeded until the end. Meanwhile, the application of bio-based concrete, the bacteria will die when the cells become embedded by $CaCO_3$ crystals and the bacteria will die when all nutrients inside concrete consumed.

2.2.1.3 Polymer Modified Concrete Healing

Polymer Modified Concrete (PMC) is made by the dispersion of organic polymers inside the mixing water of concrete. Upon cement hydration, coalescence of polymers appeared which form the concrete. Its healing mechanisms actually quite similar with the traditional concrete; but the extended over longer period compared to traditional concrete since more unhydrated cement still embedded inside whole of the matrix because polymer acted as a membrane to enclose the cement particles.

Katsuhata et al. (2001) investigate the properties of PMC containing epoxy resin without hardener and claimed it self-healing efficiency since there was regain of mechanical properties upon crack formation, the unhardened epoxy resin inside the drops filled the cracks and hardened upon contact with hydroxide ions and alkalis inside concrete. Yuan et al. (2010 & 2011) proposed mixing the Ethylene Vinyl Acetate (EVA) copolymer particles into the matrix. The specimens were heated up to 150˚C upon crack formation and Yuan et al claimed that the EVA particles melted and the adhesive flew toward the crack region and filled.