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APPLICATION OF NANOMATERIALS IN PRODUCTION OF SELF-SENSING CONCRETES: CONTEMPORARY DEVELOPMENTS AND PROSPECTS

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In the recent years structural health monitoring (SHM) has gathered spectacular attention in civil engineering applications. Application of such composites enable to improve the safety and performance of structures. Recent advances in nanotechnology have led to development of new family of sensors – self-sensing materials. These materials enable to create the so-called "smart concrete" exhibiting self-sensing ability. Application of self-sensing materials in cement-based materials enables to detect their own state of strain or stress reflected as a change in their electrical properties. The variation of strain or stress is associated with the variation in material's electrical characteristics, such as resistance or impedance. Therefore, it is possible to efficiently detect and localize crack formation and propagation in selected concrete element. This review is devoted to present contemporary developments in application of nanomaterials in self-sensing cement-based composites and future directions in the field of smart structures.

Keywords: concrete, nanomaterials, review, self-sensing

1. INTRODUCTION

Concrete structures, such as buildings, bridges and pavements, deteriorate as a result of strain/stress, cracking, delamination and other damages. Early and precise detection of damages during the exploitation of structures enables preventing further degradation and thus limiting the cost of

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necessary repairs. It is widely recommended that the critical elements of particular importance should be monitored continuously and automatically [1]. Therefore, various methods have been developed to monitor the performance and state of the concrete structures. To improve the safety of structures, structural health monitoring (SHM) allowing continuous monitoring became very interesting feature while compared to traditional non-destructive testing methods (NDT). SHM is normally performed by measuring the strain/stress in key structural locations, using the embedded strain sensors, like optical fiber sensors, electrical resistance strain gauges and piezoelectric ceramics (Fig. 1). Actually, SHM is not only the new and improved way to make a non-destructive evaluation of the structure, but it also involves integration of sensors, smart materials, data transmission and processing ability inside the structures [2, 3]. SHM is still very interesting research field and various projects are held to develop this field of science. In Poland, large number of high quality research works has been done by Institute of Fundamental Technological Research of Polish Academy of Sciences within already finished MONIT - „Monitoring of Technical State of Construction and Evaluation of its Lifespan" project and currently running "Smart Technologies for Transport Safety - Innovation Cluster Nesting (Smart-Nest)" project. SHM shows many advantages, however, these techniques suffer from high cost (expensive analysis equipment), poor durability, low survival rate, low sensitivity, and unfavorable compatibility with concrete structures [4]. These drawbacks have motivated scientists and industrial researchers to develop new generation of sensors that is better fit to the concrete structures.

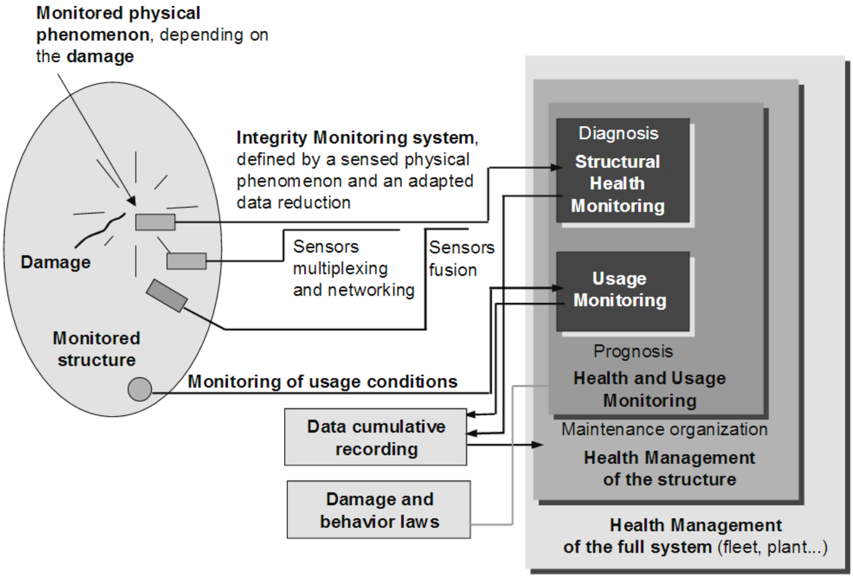

Fig. 1. Principle and organization of SHM system [3]

Recent advances in nanotechnology have led to development of new family of sensors – self-sensing materials. These materials enable to create the so-called "smart concrete" exhibiting self-sensing ability. Application of self-sensing materials in cement-based materials enables to detect their own state of strain or stress reflected as a change in their electrical properties. The variation of strain or stress is associated with the variation in material's electrical characteristics, such as resistance or impedance. Therefore, it is possible to efficiently detect and localize crack formation and propagation in selected concrete element [5]. The concept of smart concrete is based on the idea from the last decade devoted to application of fibers in concretes (FRC – fiber reinforced concrete), which enabled sensing the strain by piezoresistivity or sensing damage by utilizing the relation between damage and electric resistance [6]. Nanomaterials, due to ultrafine size of particles, show unique physical and chemical properties, different from those of the conventional materials [6]. This is due to the remarkable mechanical and electrical properties of some nanomaterials, which make these nanoparticles ideal for manufacturing self-sensing cement-based composites [5]. Cementitious materials exhibit poor or no electrical conductivity and incorporation of well-dispersed nanomaterials in a concrete matrix enable to form an extensive conductive network inside the concrete. Amount of required nanomaterial to be incorporated depends on the type of nanomaterial and its properties. In general, the minimum dosage of admixture that creates conductive pathways is known as percolation threshold [7]. Briefly, it can be defined as the critical fraction of lattice points that must be filled to form a continuous electrical path along the cement matrix [8]. However it is not entirely necessary to reach the percolation threshold (high conductivity is not needed for strain sensing applications). Studies have shown that incorporation of nanomaterials above the percolation threshold is beneficial for the sensing sensitivity under tension, and incorporation of nanomaterials below the percolation threshold is beneficial for the sensing sensitivity under compression [9]. Besides, self-sensing properties application of nanomaterials contributes to strength and microstructural improvements [10, 11, 12]. In addition, due to the fact that the sensor and concrete are both homogeneous material it will show good compatibility and same service life as the structure [4].

This review is devoted to present contemporary developments in application of nanomaterials in self-sensing cement-based composites and future directions in the field of smart structures.

2. TYPES OF NANOMATERIALS

For enabling self-sensing ability of cement-based structures, various materials (so-called functional fillers) can be applied. The “smart concrete” belongs to the new generation of structure materials developed from fiber reinforced concrete. Therefore, carbon fibers (CF) and steel fibers (SF) were previously applied. From among the macro- and microscale materials, graphite powder (GP), nickel powders (NP) and steel slag (SS) were also incorporated. Recent development of nanotechnology enabled to synthesize other materials, which can be used, such as: carbon nanofibers (CNF), carbon nanotubes (CNT), graphene oxide (GO), titanium dioxide (TiO_2) and Fe_2O_3, carbon black (CB) [9]. The list of materials is not closed and various materials can be applied as soon as they are well-dispersed in a concrete matrix and can create extensive conductive network inside concrete. Functional fillers can be grouped to different categories which are related to their shape, scale, conductive capability, application type or material component (Fig. 2).

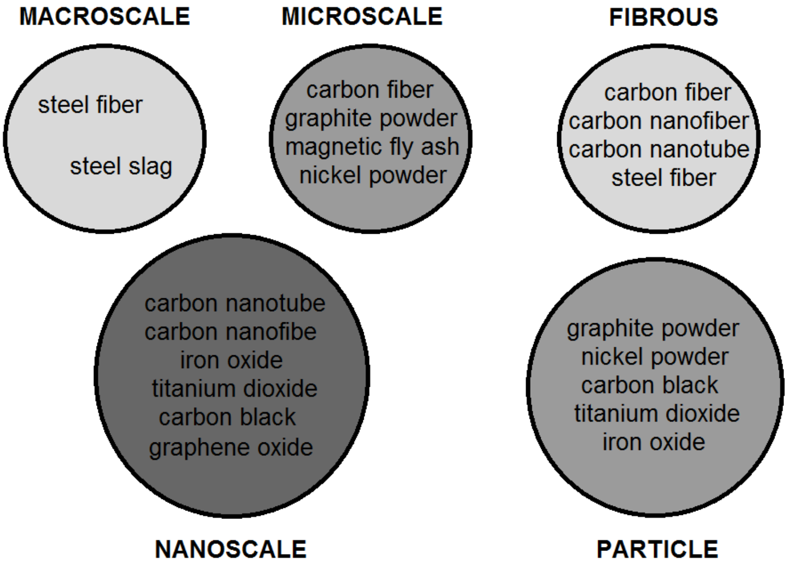

Fig. 2. Example of materials used in relation to their scale and shape

Both particle and fibrous particles have their benefits and disadvantages. Fibrous fillers due to high aspect ratios (ratio of length to diameter) can be very beneficial for self-sensing properties at lower concentration while compared to the particles, although the fibrous materials are more difficult to disperse and have tendency to be damaged during the preparation of composite (mixing process). Incorporation of functional fillers does not have to be restricted to one filler, application of the hybrid fillers is preferable in order to exhibit properties, which cannot be achieved by any of the single fillers alone. However, in that case the proper dispersion and content should be considered. For example, when CNFs–CNTs are used to reinforce any kind of material, those nanomaterials strongly attract each other due to van der Waals forces. As a result, agglomeration is observed with formation of entangled threads and clumps (which are very difficult to disentangle) [13]. Proper dispersion of the nanomaterials is a key issue in order to apply them efficiently in self-sensing cement-based composites [14]. Fiber-bridging effect and the clustering of the electrically conductive fibers make it difficult to be adopted in manufacturing of damage self-sensing material [15]. Possible creation of clumps of nondispersed nanomaterials highly affecting the sensing properties (Fig. 3).

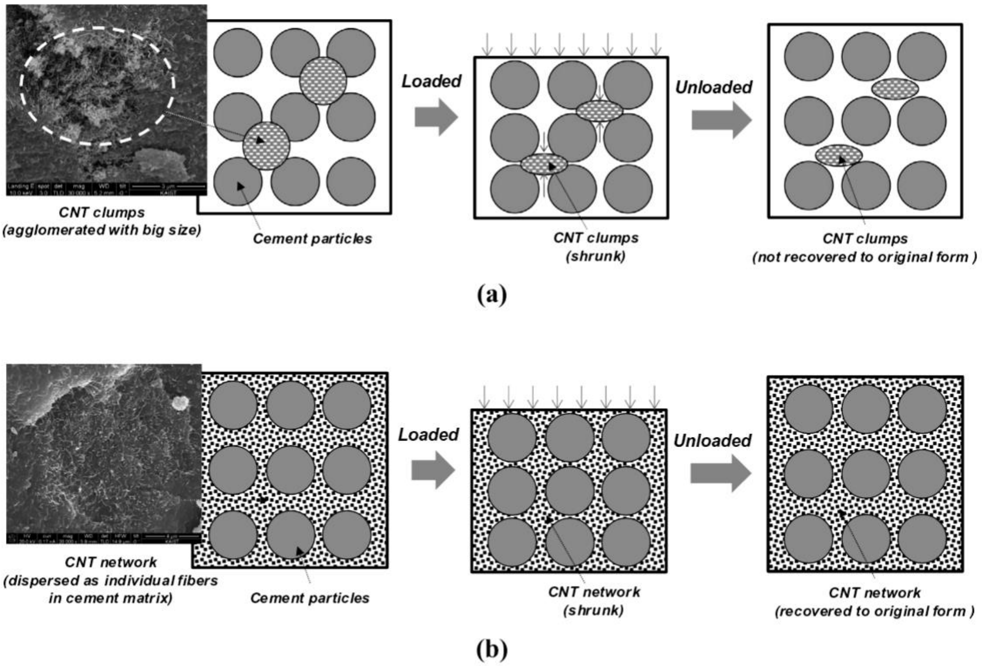

Fig. 3. Schematic illustration of the morphological change of CNT/cement composite matrix after loading and unloading: the cases of poor dispersion of CNTs (a) and good dispersion of CNTs (b) [16]

To overcome this obstacle, incorporation of dispersing materials is recommended. Three main benefits of using dispersing materials are:

1) possibility to obtain reproducible and stable sensing and mechanical properties,
2) improvement of filler efficiency (resulting in decrease of necessary concentration level of the filler),
3) decreasing of consumption of mechanical energy for mixing [17].

Among the dispersants mainly two types of materials are used: surfactants and mineral admixtures. Dispersion capability of surfactant depends on its composition and can be achieved by wetting, electrostatic repulsion and/or steric hindrance effects [18]. In the case of mineral admixtures, the result is attributed to gradation, adsorption and/or separation effects.

Besides the chemical methods, also various mechanical methods, like milling or ultrasonication, are simultaneously adopted [19, 20]. Many works have been made in order to find both proper and economically reasonable surfactants [20]. Various surfactants have been tested by many researchers. However, due to the nature of the cement-based materials, some of the effective surfactants used in the chemical industry are not compatible with cementitious materials and might contribute to alteration of mechanical and microstructural properties of composites. Therefore, further investigation of the effects of surfactants on the mechanical and electrical properties as well as durability of cement based materials are required. The compatibility between surfactants and cement should be also addressed [21].

In the light of the aforementioned facts the main approach is to adopt commonly used admixtures, such as water reducing admixtures, as surfactants. Besides their possibility to disperse nanomaterials, they are also effective in improving the dispersion of cement particles, hence improving the uniformity and workability of nano-modified cement composites [21]. Studies related to the influence of polycarboxylate superplasticizer have shown that CNTs and CNFs can be effectively dispersed in cement matrix this way, therefore, nanocomposites with strong piezoresistive characteristics can be successfully manufactured with the use of the typical admixtures [14].

3. METHODS OF PRODUCTION AND TESTING

In the literature, there are available few methods of manufacturing samples for testing self-sensing properties of nanomodified cement-based composites. They are differentiated due to the structural type of sample, size of sample and type of the test. In general, electrodes can be attached or embedded to the sample. The first method has its advantage in not affecting the sample, however, its practical application is moot due to easy way to debond the electrode. The second possibility is to embed the electrodes (mesh, perforated plate or loop electrode), thus it will be integrated and protected in the composite [17].

The arrangement of the test specimens is always dependent on the given method of testing [22], therefore, the preparation of self-sensing composite samples and number of attached/embedded electrodes is dependent on the method of testing of self-sensing properties. Two main, relatively simple, methods are applied for this purpose: the two- and four-probe methods (Fig. 4). The two-probe method employs two electrodes at the end of the specimen; they pass the current through the cement matrix. The four-probe method consists of four electrodes, which allows for two inner contacts to pass the electrical current and two outer contacts to detect the voltage between those points [17]. Furthermore, alternating current or direct current can be used for investigating conductivity.

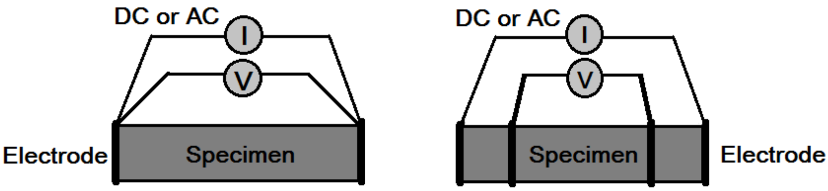

Fig. 4. Conductivity measurement based upon a) 2-point probe and b) 4-point probe technique

There are five possible methods of manufacturing self-sensing concrete structure for structural health monitoring:

- bulk form,
- coating form
- sandwich form,
- bonded form,
- embedded form.

Among these forms, the production of self-sensing concrete in bulk form (entire mass of composite) is the simplest way, however, this method is economically least efficient. Because the SHM is necessarily used only in key points of the structure, in coating or sandwich form only one or two surfaces (sandwich form) of structure are covered with the layer of self-sensing concrete. In bonded and embedded form small sensors, containing functional fillers, are prepared (prefabricated) and attached or embedded to the structure. The later four forms are more complicated in application, but can be beneficial due to the fact that they do not contribute to steel corrosion, which can be caused by the electrical conductivity of self-sensing concrete [9, 17].

4. SUM UP; FUTURE DIRECTIONS OF DEVELOPMENT

So far, self-sensing materials find their application mostly in traffic detection and SHM of buildings and bridges. Its potential application covers also the security and military structures. However, there is still lot of work required in order to develop some proper guidance and specifications enabling to uniform all the properties of such materials.

Despite very promising results regarding incorporation of nanomaterials to production of self-sensing concretes, there are still some disadvantages, which need to be resolved in order to promote the development of self-sensing concretes.

Firstly, proper method of incorporation of nanomaterials, enabling uniform dispersion leading to decreasing of the content of functional filler, is required. Due to the fact that functional filler is the most expensive component in the composite it is required to find some simple and repeatable low-cost method [17]. Besides the proper dispersing method, preparation of new functional fillers or hybrid fillers can contribute to the development in this field of science. In the last years graphene oxide [23, 24] and graphene nanoplatelet [15, 25] have gathered spectacular attention as a potential material to improve self-sensing ability of cement-based materials. The entanglement of carbon nanotubes represent some major challenge for large-scale structural application. Incorporation of graphene, which is a flat sheet of carbon atoms with only one atom thickness, might be the next step towards development of self-sensing concretes. Planar structure of graphene sheets provides much larger contact area since the top and bottom surfaces of the graphene sheet are in close contact with the host material. In addition, the superior aspect ratio (the ratio between length and width) is much higher than those of CNTs and conventional fibers [26]. Moreover, it was observed that in this case even very small amounts (0.05% or 0.1%) can be much more effective than application of standard CNTs [23, 26]. However, the large surface forces of graphene oxide enforce researchers to find proper method of uniform dispersion of graphene in composite.

Besides the simple "hybrid" application method, consisting in the introduction of various functional fillers as a separate materials, the new promising direction of synthesis a hybrid structures has been introduced recently. The latest study related to the manufacturing of hybrid fillers containing CNT and graphene has shown that incorporation of such filler significantly improves the performance of epoxy based composites as compared to the single materials added to the composite [27]. Therefore, it is possible to synthesize the nanocomposite with superior properties.

Another challenge for the progress in this field is related to the testing methods of self-sensing composites. In laboratory applications two- or four-probe methods using simple electrodes can be successfully applied, however, in practical application the signal can be affected by noises and other environmental uncertainty. Moreover, various environmental factors such as chlorides, humidity, elevated temperature, etc., might affect the results. Therefore, a development of measurement methods and equipment (i.e. electrodes) is necessary. Additionally, it has to be taken into account that self-sensing concrete in the real structure is not subjected to only one type of stress, like in laboratory conditions. Hence, the universal model describing properties of self-sensing concretes along with the proper sensing testing procedure is necessary [17].

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ZASTOSOWANIE NANOMATERIAŁÓW DO WYTWARZANIA BETONU ZDOLNEGO DO AUTODETEKCJI USZKODZEŃ: STAN OBECNY I PERSPEKTYWY

Słowa kluczowe: autodetekcja, beton, nanomateriały, przegląd

STRESZCZENIE:

Obiekt budowlany powinien spełniać wymagania bezpieczeństwa, trwałości i niezawodności dla długotrwałego funkcjonowania. Monitorowanie obiektu umożliwia kontrolowanie jego bezpieczeństwa i trwałości w trakcie całego cyklu życia budynku. Wczesne i precyzyjne wykrycie uszkodzeń, powstających w trakcie użytkowania obiektu, może umożliwić właściwe działania prewencyjne i naprawcze oraz utrzymanie nieprzerwanej eksploatacji obiektu. Rozwój innowacyjnych automatycznych systemów monitoringu technicznego konstrukcji - MTK (ang. Structural Health Monitoring, SHM) pozwala na zastąpienie tradycyjnej diagnostyki, opartej na badaniach nieniszczących NDT (ang. non-destructive testing). Podstawową zaletą systemu MTK jest nieprzerwany monitoring stanu obiektu budowlanego, pozwalający na ocenę obciążeń, szybkie wykrywanie zmian i uszkodzeń w badanej strukturze wraz z obserwacją ich rozwoju oraz ocenę zagrożeń z nimi związanych. Ponadto, zastosowanie nowoczesnych technik monitorowania pozwala na znaczną redukcję kosztów spowodowanych okresowymi inspekcjami. Niestety, zastosowanie MTK niesie ze sobą koszty związane z drogą aparaturą pomiarową; wymaga także rozwiązania trudności związanych z niekiedy niewystarczającą trwałością i czułością urządzeń oraz możliwą niekompatybilnością z elementami betonowymi. Niedogodności te przyczyniły się do poszukiwania nowej metody pomiarowej, pozwalającej na przynajmniej częściowe przezwyciężenie niedogodności związanych z klasyczną metodą monitorowania technicznego konstrukcji.

W ostatniej dekadzie rozwój nanotechnologii pozwolił na produkcję wzmocnionych struktur kompozytowych ze zdolnością do monitorowania konstrukcji. Zainteresowanie takimi układami wykazuje również budownictwo, gdzie konstrukcje inżynierskie podlegają ciągłemu wpływowi nie zawsze przewidywalnych czynników zewnętrznych, a od parametrów technicznych materiałów zależy w dużym stopniu bezpieczeństwo użytkowania obiektów. Nanomateriały, ze względu na swoje właściwości i parametry fizyczne, mogą znacznie poprawiać właściwości mechaniczne kompozytów, a ponadto niektóre z nich posiadają unikatowe właściwości przewodności elektrycznej. Pod tym względem, ich wydajność i właściwości są lepsze od konwencjonalnych domieszek i dodatków. Zastosowanie nanomateriałów jako domieszek pozwala na wytworzenie mieszaniny izolatora i przewodnika. Kompozyt cementowy zawierający domieszkę nanomateriału zaczyna wykazywać właściwości piezorezystywne, to znaczy zmienia swój opór właściwy wraz z odkształceniem. Materiały takie można nazwać kompozytami „inteligentnymi", gdyż umożliwiają one autodetekcję uszkodzeń. Pod wpływem odkształceń mechanicznych kompozytu cementowego, w którym znajduje się monitorowany nanomateriał, może następować wzrost oporności sieci przewodzącej. Zmiany oporności są efektem zmian w nanostrukturze, a także w przestrzennym ułożeniu nanomateriałów względem siebie. Zjawisko to pozwala na monitoring właściwości mechanicznych kompozytowego materiału, gdyż analiza odpowiedzi elektrycznej (zmian oporności) pozwala ma wykrycie ewentualnych defektów lub poważnego zniszczenia materiału. Odpowiednia precyzja i czułość w monitorowaniu pracy kompozytu cementowego jest zależna od kilku właściwości nanomateriałów, przede wszystkim morfologii (kształt, rozmiar, długość, stan powierzchniowy, stopień agregacji i aglomeracji) oraz od zawartości nanomateriału w kompozycie.

Istnieje kilka metod umieszczania inteligentnego kompozytu w badanym elemencie konstrukcyjnym. Nanomateriał może zostać umieszczony w całej masie kompozytu, może także stanowić pokrycie danego elementu, jednostronne lub punktowe bądź obustronne (tzw. metoda „sandwich”). Ponadto, sensory mogą zostać wbudowane w element lub doczepione do elementu konstrukcyjnego. Pokrycie danego elementu warstwą/warstwami lub wbudowanie/doczepienie sensorów pozwala osiągnąć lepszą wydajność monitorowania i obniżyć koszty konstrukcji (ponieważ monitorowanie konstrukcji jest niezbędne tylko w newralgicznych miejscach). Natomiast zastosowanie nanomateriału w całej objętości kompozytu jest o wiele prostsze do wykonania.

Monitorowanie stanu konstrukcji odbywa się przez pomiar rezystancji metodą dwupunktową lub metodą czteropunktową. W zależności od sposobu umieszczania styków elektrod i sposobu zbierania sygnału możliwe jest uzyskiwanie pomiaru punktowego lub polowego na całej powierzchni kompozytu, a nawet w jego przekroju.

Pomimo bardzo dobrej skuteczności i obiecujących rezultatów badań, wdrożenie tego typu inteligentnych kompozytów cementowych wymaga wciąż jeszcze rozwiązania licznych problemów. Po pierwsze, konieczne jest opracowanie sposobu prawidłowego wprowadzania nanocząstek do kompozytu cementowego, tak aby unikać powstawania skupisk aglomeratów, które mają bardzo niekorzystny wpływ na zdolność monitorowania właściwości kompozytu. Ponadto, prawidłowe zdyspergowanie nanomateriału w matrycy cementowej umożliwi zmniejszenie ilości wymaganej domieszki, czego skutkiem będzie zmniejszenie kosztów produkcji.

Odnośnie do typów stosowanych nanomateriałów, konieczne jest poszerzenie stanu wiedzy na temat stosowania ich mieszanin lub syntezy nowych hybrydowych nanostruktur, łączących właściwości włókien i cząstek. Układy hybrydowe mogą pozwolić na zmniejszenie niezbędnej ilości domieszki nanomateriału przy zachowaniu odpowiednich parametrów kompozytu. Potrzebna jest także odpowiednio zaawansowana metoda pomiaru właściwości „inteligentnego” kompozytu cementowego; metody laboratoryjne nie nadają się do praktycznych zastosowań ze względu na dużą liczbę zakłóceń ze strony środowiska. Wreszcie, należy opracować uniwersalny model, opisujący właściwości kompozytu i pozwalający na prawidłową interpretację wyników pomiarów.