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In-Situ Triboluminescent Optical Fiber Sensor for Real-Time Damage Monitoring in Cementitious Composites

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IN-SITU TRIBOLUMINESCENT OPTICAL FIBER SENSOR
FOR REAL-TIME DAMAGE MONITORING IN CEMENTITIOUS COMPOSITES

By
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This work is dedicated to:

Jesus Christ my Lord, Redeemer and Shepherd for He has never failed, lied or lost a battle;

My beloved parents – Engr (Late) and Mrs Adeoye O. OLAWALE;

God’s priceless gift of love, favor and wisdom to me: Martha(mi) Oluwasheyi OLAWALE;
“Many women do noble things but you surpass them all.”
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ABSTRACT

Triboluminescent-based sensor systems have the potential to enable in-situ and distributed structural health monitoring of composite structures. Inability to effectively capture and transmit optical signals generated within opaque composites like concrete and carbon fiber reinforced polymers have however greatly limited their use. This problem is being addressed by the development of the bio-inspired in-situ triboluminescent optical fiber (ITOF) sensor. This sensor has the potential for wireless, in-situ, real-time and distributed (WIRD) damage monitoring. Its integrated sensing (triboluminescent thin film) and transmission (polymer optical fiber) components convert the energy from damage events like impacts and crack propagation into optical signals that are indicative of the magnitude of damage in composites.

Utilizing the triboluminescent (TL) property of ZnS:Mn, the ITOF sensor has been successfully developed. Key design parameters were evaluated to develop a sensor with enhanced damage sensing capability. Material properties of the new sensor were characterized with Raman spectroscopy, field emission scanning electron microscopy (FESEM) and dynamic mechanical analysis (DMA). Flexural tests were also carried out to evaluate the damage sensing performance of the sensor before integrating into unreinforced concrete beams to create triboluminescent multifunctional cementitious composites (TMCC) with in-situ damage monitoring capabilities like biological systems.

Results show that the ZnS:Mn in the epoxy coating of the ITOF sensor does not degrade the thermo-mechanical properties of the composite system. Raman spectroscopy indicates that the ZnS:Mn crystals retained their physical and chemical properties after undergoing the sensor fabrication process. Enhanced side coupling of TL signals from the ITOF coating into the polymer optical fiber (POF) was achieved with TL thin film coating on POF. This makes distributed sensing possible when the entire length of the POF is coated with TL thin film. Uniform TL crystals dispersion and uniform coating of the sensor are critical for consistent sensor performance. A new approach to damage characterization using TL emission profiles was employed with the TMCC. Three modes of sensor excitation in the TMCC were identified indicative of sensor’s ability to sense crack propagation within the beam. FESEM analysis indicated that fracto-triboluminescence was responsible for the TL signals observed at beam failure. The TL profile analysis promises to facilitate better understanding of crack propagation in composite structural materials.
CHAPTER ONE
INTRODUCTION

Bridges occupy a critical position in the infrastructural system of any nation. The National Bridge Inventory (NBI) reveals that there are 591,707 bridges over 6.1 meters (20 feet) in total length located on public roads in the United States. These bridges have a total deck area of more than 300 million square meters, and carry an average of nearly 4 billion vehicles per day [1]. However, about 25% of the bridges are either structurally deficient or functionally obsolete [2]. This is due to the destructive effect of de-icing salts, pollutants, material aging, increasing traffic volume, and overloading bridges are continuously subjected to [3]. Structurally deficient or functionally obsolete bridges pose great risks to the life of commuters because limited resources militate against their replacement or prompt repair. The average age of structurally deficient bridges in the US is 59 years [4]. Over 50% of US bridges are more than 60 years old. Hence, it is estimated that the number of deficient bridges would grow by about 7600 per annum [3].

Furthermore, a study of over 500 bridge failures in the US between 1989 and 2000 showed that the most frequent causes of bridge failures were floods and collisions [5]. Flood and scour were responsible for about 60 percent of collapses (Figure 1.1) while Bridge overload and lateral impact forces from trucks, barges/ships, and trains constitute 20% of the total bridge failures [6, 7]. About 500,000 of the approximately 600,000 bridges in the US lie over water [7, 8].

Figure 1.1: Causes of bridge failures [7].
A number of catastrophic bridge failures have occurred over the past decades that have provoked interest in the development of structural health monitoring (SHM) systems for bridges and other civil infrastructure systems (CIS). An example is the collapse of the Minneapolis I-35W Bridge (Figure 1.2) in the United States on August 1, 2007. A total of 13 people died while 145 were injured. According to the National Transportation Safety Board (NTSB), undersized gusset plates, increased concrete surfacing load, and weight of construction supplies/equipment were the cause of the bridge collapse. SHM can however help to prevent sudden failure through early damage detection and prompt repairs.

Figure 1.2: Collapse of the Minneapolis I-35W bridge [9].

The structural health monitoring of concrete bridges is particularly of great importance. The combined market share for reinforced and prestressed concrete bridges in the U.S. is about 70% of bridges built since 1980 [10]. As illustrated in Figure 1.3, the NBI indicates that the combined number of concrete and prestressed concrete bridges superstructure out-number all other construction materials not just in terms of the number of bridges, but also in terms of the average distance travelled (ADT) and the deck area. This trend is expected to continue because of concrete’s economic competitiveness, relatively long life and low maintenance requirements [11].

Other than earthquakes, the most severe damage to large concrete structure arises from the corrosion of the embedded steel reinforcements especially due to deicing salt [6, 12]. The direct cost of metallic corrosion in the U.S. is estimated at $300 billion per year [13]. The degradation
of these concrete structures occurs through the formation and propagation of cracks [14]. Crack openings above 0.2-0.4 mm (depending on environmental exposure) may result in durability problems because of steel reinforcement corrosion. Larger crack openings (1-2 mm) that may be caused by excessive loading during natural hazards like earthquake are signs of severe damage that may require immediate closing of the facility [14]. There are currently no quantifiable methods to determine if buildings are safe for reoccupation after a significant earthquake [15]. Hence, monitoring cracks in concrete is an effective way to assess the structural condition or ‘health’ of a concrete structure [16, 17].

![Figure 1.3: Percentage of superstructure material types for US bridges by a. Numbers, b. Average distance travelled, c. Deck area [1].](image)

1.1 Technical Challenges

There are currently a number of techniques being used for damage detection and monitoring of cementitious composites like concrete structures [18, 19]. These include imaging techniques such as ultrasonic C-scan, x-ray and thermography. The major drawback of these techniques is that they do not provide for in-situ sensing. This inhibits the real-time monitoring of the structure. Furthermore, the associated costs resulting from the downtime required for periodic non-destructive inspections can be very high for civil structures like bridges [20]. The acoustic emission technique is promising, but it suffers from low-signal-to-noise ratio. Surface-mounted resistive foil strain gages have potential for in-situ and continuous monitoring. They are however
less effective in monitoring internal damage and are vulnerable to electromagnetic and electrical interference, as well as physical damage [18].

Triboluminescence-based sensor systems have the potential to enable *in-situ* and distributed structural health monitoring of composite structures [21]. Triboluminescence (TL) is the emission of light from solids when stressed or fractured [22, 23]. There have been a number of attempts to apply the TL phenomenon for damage sensing in composite structures [24-27]. Nonetheless, a major challenge militating against TL-based sensor systems is the inability to effectively capture and transmit the optical signal generated within opaque composites like concrete and carbon fiber reinforced polymers. A number of other factors are critical to the effective implementation of TL damage sensing. These include the effective dispersion of TL materials and the determination of optimized concentration levels in the host materials. A common approach being employed is to incorporate the TL crystals into the host material like concrete. The concentration level of the TL crystals in the host matrix required for good TL response is however, usually high. This introduces parasitic weight effect that is highly undesirable. The crystals may also adversely affect the mechanical properties and performance of the host structure. The high cost of the crystals also makes this approach not to be economically viable.

In summary, the problem is how to have an *in-situ* TL-based sensor system in opaque structures/materials like concrete with effective light transmission and detection without adversely affecting the performance of the host structure or material.

### 1.2 Research Objectives

The goal of this research is to apply the TL phenomenon of ZnS:Mn and light propagation in polymer optical fibers for the *in-situ*, continuous and real time monitoring of damage (cracks) in cementitious composite (CC) structures. This work will focus on mortar. In line with this goal, the research objectives are:

i. Investigate the viability of *in-situ* TL-based damage sensing in mortar by direct dispersion of ZnS:Mn in the host matrix

ii. Develop a triboluminescent signal transport mechanism
iii. Determine sensor’s key design parameters that give enhanced TL signal transport performance

iv. Develop fabrication methodology for the triboluminescent-based multifunctional cementitious composites with integrated TL transport mechanism and characterize *in-situ* damage sensing performance under flexural loading

v. Model TL response of the sensor under impact loading and validate proposed model against experimental data

### 1.3 Structure of the Dissertation

The dissertation is divided into eight chapters. Chapter 1 is the introduction and focuses on the motivation and key objectives of this study. Chapter 2 is the literature review and provides an update on progress in the understanding and application of triboluminescence for damage monitoring in composites. Chapter 3 presents the results of the first application of the triboluminescent properties of ZnS:Mn for damage monitoring in cementitious composites that involves the direct dispersion of ZnS:Mn in mortar matrix. The development of the bio-inspired *in-situ* triboluminescent optical fiber (ITOF) sensor is described in chapter four. Chapter 5 presents the ITOF sensor impact excitation model and its validation. In chapter six, flexural tests and some characterization tools were employed to gain insights into the properties of the ITOF sensor and its behavior under flexural loading. Chapter 7 gives the details of the fabrication and damage characterization of the triboluminescent multifunctional cementitious composites (TMCC) under flexural loading. Finally, the conclusion is provided in chapter eight.
CHAPTER TWO

LITERATURE REVIEW

This chapter provides insight into the crack mechanism in concrete structures. The underlying mechanism of the triboluminescence phenomenon and progress made in the development of triboluminescent-based sensors for damage monitoring in composite structures are discussed.

2.1 Cracks Initiation and Propagation in Concrete

Visible cracking occurs in concrete when the tensile stresses developed in the concrete system exceed the relatively low tensile strength of concrete [28]. This can be as a result of any or a combination of factors such as volume changes due to temperature and humidity gradient or crystallization pressure of salts in pores; exposure to temperature extremes; structural loading; and chemical reactions involving formation of expansive products such as in corrosion of the steel rebar [29-31]. These are illustrated in Figure 2.1. The presence of small cracks provides

Figure 2.1: Physical and chemical causes of cracking in concrete [31].
easy access for moisture and chemicals thereby accelerating concrete deterioration and structural failure. Contraction of a concrete component within a structure is always subject to some degree of restraint from either the foundation, another part of the structure, embedded reinforcing steel, or non-uniform shrinkage of the concrete [32]. Tensile stresses are developed in the concrete due to the combined effect of shrinkage and restraint that results in cracking due to the inherent low tensile strength of concrete (Figure 2.2). A typical value for the final shrinkage strain of concrete in structures is $600 \times 10^{-6}$ while the concrete tensile-strain capacity can be $150 \times 10^{-6}$ or less[32][24]. Likewise, the freezing of the infiltrated water to ice and the accompanying expansion causes deterioration either of the hardened paste, aggregate, or both due to the hydraulic and osmotic pressure developed in the pores as the water freezes and expands [28].

Concrete is however naturally resistant to corrosion. This is because the calcium hydroxide and the soluble alkalis in concrete cause the pore water solution in concrete to have a high pH ($>12.5$) which helps to protect the steel reinforcement from corrosion through the formation of a passive layer of ferric oxide on the reinforcing steel [28]. Steel tends to lose its passivity to corrosion when the Cl-/OH- molar ratio is higher than 0.6 likely because the iron oxide becomes permeable or unstable under these conditions [30]. In addition, concrete tends to hold more moisture in the presence of large amount of chloride ions. This enhances corrosion by lowering

![Figure 2.2: Cracking of concrete due to drying shrinkage [32].](image)
the electrical resistivity of the concrete. No significant corrosion is observed provided the electrical resistivity is above 50 to 70 x 10$^3$ $\Omega$.cm [30].

The corrosion of steel in concrete is an electrochemical process [30]. It requires the presence of moisture, oxygen, and an electrolyte to occur and is accelerated by wetting and drying cycles. The chemical reaction at the anode and cathode are as follows [30]:

Anode: \[ Fe \rightarrow 2e^- + Fe^{2+} \]
Cathode: \[
\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-
\]
\[
Fe^{2+} + 2(OH)^- \rightarrow FeO.(H_2O)_{nx} \text{ [rust]}
\]

The rust formed occupies a larger volume than the iron from which it was formed and depending on the state of oxidation, it may result in a volume increase as large as 600 percent of the original metal [30]. This volume increase results in internal stresses that cause cracking of the concrete and debonding between the steel rebar and the concrete [28, 30, 31]. The presence of water and moisture at the cathode is absolutely necessary to sustain the ionization of the iron at the anode and thereby sustain the corrosion process. It has been noted that the thickness of corrosion products required to cause cracking is proportional to the cover thickness; a corrosion product thickness of 50 $\mu$m (0.002 in.) is usually sufficient to cause cracking in concrete with a cover thickness of 40 mm (1.6 in.) [28].

Furthermore, laboratory studies have shown that preexisting cracks and sustained loads can accelerate corrosion initiation and propagation, and can lead to creep [33, 34]. The localized corrosion at the cracked areas lead to further longitudinal surface cracking, delamination, and debonding, ultimately resulting in a reduction in the strength capacity and stiffness of the structure [28, 35]. Table 2.1 provides recommended acceptable crack sizes for different scenarios.
Table 2.1: Guide to reasonable* crack for reinforced concrete under service loads [32].

<table>
<thead>
<tr>
<th>Exposure condition</th>
<th>Crack width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In.</td>
</tr>
<tr>
<td>Dry air or protective membrane</td>
<td>0.016</td>
</tr>
<tr>
<td>Humidity, moist air, soil</td>
<td>0.012</td>
</tr>
<tr>
<td>Deicing chemicals</td>
<td>0.007</td>
</tr>
<tr>
<td>Seawater and seawater spray, wetting and drying</td>
<td>0.006</td>
</tr>
<tr>
<td>Water-retaining structures+</td>
<td>0.004</td>
</tr>
</tbody>
</table>

* It should be expected that a portion of the cracks in the structure will exceed these values. With time, a significant portion can exceed these values. These are general guidelines for design to be used in conjunction with sound engineering judgment.

+ Excluding non-pressure pipes.

2.1.1 Strain Localization

Concrete is an anisotropic and heterogenous material made up of cement, fine aggregate, coarse aggregate, and water. The cement hydrates when mixed with water to form a hard matrix after a certain period of curing. The hydrated cement when in the fluid state flows to occupy the spaces between the aggregates and on curing acts as the binder that bonds them together.

Macroscopically, concrete can be considered a two-phase material consisting of the matrix and the aggregate [36]. However, the interfacial transition zone (ITZ), between the hardened cement paste (hcp) and the aggregate, often has more voids and is weaker compared to the bulk cement matrix. This is due to the differences in the modulus of elasticity, thermal expansion coefficient and response to change of moisture content, of the matrix (hcp) and the aggregate [30, 37]. Consequently, as the load on the concrete increases, cracking will start in the ITZ, and subsequently propagate into the hydrated cement paste until crack paths are formed through the concrete, as shown in Figure 2.3. When this is sufficiently extensive, it will result in the failure of the structure. The ITZ is about 30-50 microns wide [37].
Concrete, unlike linear elastic materials (ideally brittle) is a quasi-brittle material that exhibits substantial nonlinearity before the maximum stress. The stress-elongation relationship for a concrete subjected to uniaxial tension has been divided into four stages (Figure 2.4) [37, 38].

The first stage is before point A, which is about 30% of the peak load. At this stage, the propagation of internal voids is negligible. In the second stage (point A to point B), which is up to about 80% of the peak load, internal voids propagate.

The cracks are isolated and randomly distributed over the specimen volume, and the distribution of tensile strain in the loading direction is approximately uniform over the specimen length. In the third stage (point B and point C), the internal cracks start to localize into a major crack, which propagates with increasing load. This phenomenon is called damage localization or strain localization and causes non-uniform distribution of tensile strain over the specimen’s length in the loading direction.
Figure 2.4: Stages of crack propagation in concrete under tension [36].

The crack propagation is stable until the peak load (point C) is attained. Stable crack growth implies that the crack propagates only when the load increases [36]. The crack length at the peak load is referred to as the critical crack length. The fourth stage is after the peak load and here, the major crack continuously propagates even though the load decreases. The tensile strain of the material within the localized damage band continuously increases, whereas unloading may occur for the material outside the damage band. Consequently, the failure of concrete is characterized by strain localization that may be modeled by a macro-crack. The failure of concrete can therefore be simulated by fracture mechanics, a powerful tool to describe crack propagation [36].

2.1.2 Non-linear Fracture Mechanics for Concrete System

Linear elastic fracture mechanics is not suitable for modeling the failure of concrete because the fracture behavior of concrete is greatly influenced by the relatively large fracture process zone [36]. LEFM can be applied when the length of the fracture process zone is much smaller than the cross section dimension of the structure but this is usually not the case for most concrete structures [39]. Furthermore, the crack path in concrete is tortuous, and it is difficult to determine
the crack tip in concrete because of particles bridging and variation of the fracture process zone along the thickness direction. Hence, nonlinear fracture mechanics needs to be used in modeling concrete fracture. Some of the toughening mechanisms in the sizeable fracture process zone in concrete are shown in Figure 2.5.

An accurate description of concrete fracture needs to include the tortuous crack path, the three-dimensional aspects of the crack profile, and the inelastic material response within the fracture process zone [36]. This can be achieved by representing the crack in the structural material with an effective quasi-brittle crack. Figure 2.6 shows an effective quasi-brittle crack where an initial crack and the toughening mechanisms in the associated fracture process zone are presented by an effective crack with length (a) and a cohesive pressure σ(w) acting on the crack surfaces respectively. The cohesive pressure σ(w) tends to close the crack and is a monotonically decreasing function of crack separation displacement (w).
The value of $\sigma(w)$ at the end of the fracture process zone ($w=0$) is equal to material tensile strength $f_t$. The load on a concrete structure with the effective quasi-brittle crack results in an energy release rate $G$ at the tip of the effective quasi-brittle crack. The $G$ may be considered as the resistance to crack propagation that consists of two parts [36]: (a) the energy rate consumed during material fracture in creating two surfaces (the material surface energy) i.e. the Griffith-Irwin energy dissipation mechanism, and (b) the energy rate required to overcome the cohesive pressure $a(w)$ in the separating of the surfaces i.e. the Dugdale-Barenblatt energy dissipation mechanism. The energy release rate for a mode I quasi-brittle crack may be expressed as follows [36]:

$$G = G_{IC} + \int_0^{CTOD} \sigma(w)dw$$  \hspace{1cm} (3.2.13)$$

where $G_{IC}$ is the strain energy rate to create two new crack surfaces for mode I crack, $\sigma(w)$ is the normal traction pressure that is the function of crack opening displacement $w$ as shown in Figure 2.6, while CTOD is the original crack-tip opening displacement.

### 2.2 Crack Monitoring in Concrete Systems

Damage has been defined as changes introduced into a system that adversely affect its current and future performance [15]. Based on length-scales, all damage begins at the material level.
Such damage is usually called a flaw or defect and is present to some degree in all materials. Under appropriate loading conditions, the defects or flaws grow and coalesce at different rates to leading to component and then system-level damage [15]. Damage does not necessarily means a total loss of system functionality but that the system is no longer operating in its optimal manner. If the damage is allowed to grow, a point of failure is reached at which it is no longer acceptable to the user. On the time-scales, damage can accumulate incrementally over long period of time such as in fatigue or corrosion damage accumulation. Damage can also occur in relatively shorter time-scales such as from scheduled discrete events such as aircraft landings and from unscheduled discrete events such as military or terrorist attacks, or from natural phenomena hazards such as earthquakes [15].

Structural health monitoring (SHM) is the process of implementing a damage identification strategy for aerospace, civil and mechanical engineering infrastructure [15]. It involves the the observation of a structure or mechanical system overtime using periodically spaced measurements, the extraction of damage-sensitive features from these measurements and the statistical analysis of these features to determine the current state of the system’s health [15]. SHM usually involves online-global damage identification in structural systems such as aircrafts, buildings and bridges. Global health monitoring do not give sufficiently accurate information to determine the extent of the damage and are mostly based on either finding shifts in resonant frequencies or changes in structural mode shapes. There is lot of questions about the suitability of modal data for damage detection since modal information is a reflection of the global system properties while damage such as crack initiation and propagation is a local phenomenon [40, 41]. Furthermore, the effects of environmental changes especially temperature, can often mask subtler structural changes caused by damage [42, 43]. A combination of global and local health monitoring methods is therefore necessary for effective SHM [44, 45].

There are two major challenges for crack monitoring in concrete: exact crack locations cannot be determined a priori because of concrete’s high inhomogeneity; and there are many possible crack locations along the concrete due to the load redistribution effect of the steel reinforcements [16][]. Furthermore, all existing electrical instruments and most fiber optic sensors are ‘point’ sensors that can only detect changes at local points in a structure [16]. Such measurements are not effective for health monitoring of concrete structures since degradation of such structures
occurs through the formation and propagation of localized cracks that have little effect on structural stiffness [16, 46]. Consequently, measuring the displacement, strain or acceleration at a particular sensing point is insensitive to cracking unless the point is very close to the damage location or by using very large number of sensors which is impractical [16, 46].

In addition, the prevailing approach for evaluating the structural condition of bridges is through visual inspection and tap tests by trained personnel [2, 3]. Visual inspection and tap tests are however limited to finding voids near the surface of concrete [4]. This approach is also highly subjective and labor-intensive. It has resulted in the retrofitting or replacement of many bridges that did not warrant such attention, while increasing the possibility of failure to identify bridges needing rehabilitation or replacement [3, 4, 6].

2.2.1 Acoustic-based Damage Detection

Elastic waves in the ultrasonic frequency range are widely used in the nondestructive evaluation (NDE) of defects in concrete [47-49]. This class of acoustic based NDE techniques consists of the passive acoustic emission (AE) and the ultrasonic testing (UT) methods. The AE is an inspection technique which detects elastic waves due to micro-cracking while ultrasonic testing (UT) detects elastic waves due to impacts from a steel ball or dynamic vibrations driven by a piezoelectric element [47].

Acoustic Emission (AE)

AE is the spontaneous generation of pressure waves by a material under loading due to the sudden release of energy from micro-cracking [17, 47]. The onset of damage in a structure is preceded, and accompanied by an emission of elastic waves that spread in the material [17]. These can be received and recorded by sensors applied to the external surface and used to locate where cracks form [47]. The technique was originally employed to detect cracks and plastic deformations in metals [50] but can also be used for diagnosing structural damage phenomena in concrete and masonry structures [51-53]. The strength of AE measurement techniques is the ability to monitor microscopic damage occurring inside the material [54]. AE monitoring is performed by means of piezoelectric (PZT) sensors, using crystals that give out signals when subjected to a mechanical stress [55].
Because the amplitude of the elastic pressure waves is usually very weak, less than a millionth ($10^{-6}$) of the atmospheric pressure, the electric (voltage) signals emitted by the transducers have to be amplified greatly ($10^4$ or $10^5$ times) before processing [56]. The signal amplification value generally adopted in monitoring AE events in concrete is $60\text{dB}$ [30] and the duration of a signal emitted during the cracking of a non-metallic material, like concrete, is around $2000\mu\text{s}$ [50]. The amplified signal is then filtered to eliminate unwanted frequencies, such as the vibrations due to the mechanical instrumentation, which are generally lower than 100 kHz. The AE signals collected are composed of thousands of damped oscillations, and are analyzed by using a threshold measurer which counts the oscillations exceeding a predetermined voltage level as illustrated in Figure 2.7 [57]. This method is called the Ring-Down Counting and is widely used with the AE technique for the identification of defects [17, 55, 58, 59]. It is assumed that the counting number ($N_T$) is directly correlated to the quantity of energy released during the loading process and that its increase is proportional to the crack growth [58]. All the oscillations produced by a single AE signal are assumed to belong to a single event.

![Figure 2.7: Counting methods in AE technique [17].](image)

In their study, Carpinteri and Lacidogna [17] observed that the cumulative counting number ($N_T$) is approximately proportional to the growth of the crack and that crack arrest coincides with the damping of the significant oscillations as illustrated in Figure 2.8. The emission rate confirms
that the maximum number of oscillations coincides with the maximum growth rate of the crack [17]. As a result, a deceleration takes place and both the counting rate and the crack velocity rapidly decreased to zero. The final stage showed a stable behavior.

Figure 2.8: Crack monitoring with AE [17].

**Ultrasonic Testing (UT)**

The most commonly used stress wave methods for detecting defects in concrete are the pulse-echo, and impact-echo methods [60]. Flaws and delaminations are detected through the reflection of the transmitted stress wave which is detected by a receiver [60]. However, their application in heterogeneous materials such as concrete has been limited due to attenuation of stress waves within the material [60]. Furthermore, condition monitoring of bridges with these methods require point-by-point interrogation of concrete decks which is not cost effective and is time consuming in practice [60]. The pulse-echo methods further suffer from two main limitations. Firstly, the steel reinforcement usually contained in concrete structural members prevents defects from being detected in the regions that they shadow [61]. Secondly, the depth at which embedded cracks can be detected is rather poor. It is limited to detecting horizontal cracks of 5 cm length at a depth of 14 cm and rapidly loses this ability with the inclination of the cracks [44].

Chen and Ansari [60] developed a methodology based on the interferometric detection of ultrasound using optical fibers. They claimed that many fiber optic acoustic sensors have been developed that exhibited higher sensitivities than PZT based sensors. A brief review of work on fiber optic acoustic sensors is given in [60].
The use of mechanical impact to generate the stress pulse has the greatest success in concrete testing in practice and several of such techniques have been developed [54, 62-71]. The impact echo method was developed in the 1980s by Sansalone and Carino [67] for the detection of flaws in relatively thin concrete structures [62, 71]. The method has been successfully used in detecting voids and honeycombed concrete in members, delaminations in bare and overlaid slabs, and voids in tendon ducts [62, 72-74]. The first standard on the use of the impact-echo method for thickness measurement was adopted in 1998 by the ASTM [62, 67].

When carrying out an impact-echo test, a transient stress pulse is introduced into the test object using a mechanical point impact as shown in Figure 2.9. The stress waves generated travel in to

![Figure 2.9: The impact echo method [68].](image)

object along spherical wavefronts as compression (P) and distortional (S) waves [68, 75]. A surface wave (R) also travels away from the impact point. The P- and S-waves are reflected by internal defects (difference in acoustic impedance) or external boundaries [62, 71] and are measured using a displacement, velocity or acceleration transducer [63, 75]. From the pulse velocity $C_p$ through the specimen and the measured arrival time $t$ of the reflected wave, the distance $T$ to the target can be calculated [68]:

$$T = \frac{C_p \cdot t}{2}$$
The development and use of frequency analysis in place of the time domain analysis contributed greatly to the success of the impact echo method [68]. The recorded surface displacement waveform is transformed into the frequency domain for easier analysis by using the fast Fourier transform technique. The waveform has a dominant frequency, \( f \) that corresponds to the plate thickness frequency. It is the inverse of the measured arrival time \( t \) and is given as [62, 68, 75]:

\[
\frac{C_{pp}}{2T} = \frac{C_{pp}}{2T} \quad (2.2)
\]

Where \( C_{pp} \) is the P-wave speed through the thickness of the plate. Equation (2.2) is the basic relationship for interpreting the results of impact-echo tests [68].

### 2.2.2 Electromagnetic Imaging Methods

Some of the imaging methods that have been adopted and validated for the assessment of concrete bridge conditions include Thermography, Ultrasonic Pulse Velocity (UPV), and Ground Penetrating Radar (GPR) [76]. Thermography method uses infrared cameras to detect thermal differences in the bridge deck to produce images that are analyzed for defects location. Infrared thermography is limited by environmental conditions and has difficulty evaluating decks with asphalt overlays [62]. In UPV, ultrasonic waves are sent into the bridge deck where they are reflected when they hit interfaces/defects. The received reflected signals are then transformed into images for further analysis and defect location. UPV has been found to be very effective for steel structures but not as effective in concrete structures due to the high attenuation of concrete [76].

GPR is perhaps the most attractive and promising of the NDE methods available for the detection of deteriorations in concrete bridge decks, especially where the results are presented in image format [62, 76, 77]. This is because GPR systems can collect vast amounts of data at high speed and identify various defects in structures [62, 76]. However, existing GPR systems require significant expert analysis to effectively evaluate deck condition, and have had difficulty providing fast and reliable results that satisfy the needs of state highway agencies [62, 76, 78].
some cases, the interpretation of GPR images requires additional information from destructive methods such as coring or drilling [79].

**Ground Penetrating Radar (GPR)**

A GPR system emits radar (Radio Detection and Ranging) and radio waves from an antenna into a structure to detect defects [76]. When the radar and radio waves come in contact with a defect, some of the energy is re-emitted and this is used to detect the defect and to determine its size, direction, distance and properties [80]. GPR provides images that relate the amplitude of the signal to the arrival time or depth when the velocity in the medium is known [81]. The image of the subsurface is obtained by assigning a different color to each amplitude and combining the traces [76]. From the permittivity of the material (dielectric constant); the speed of the electromagnetic impulse can be calculated and the depth of reflectors (defects/interfaces) can be determined. The velocity of the traveling electromagnetic pulse within the medium is given by equation (2.3) [81] while Equation (2.4) is used to determine the value of the relative dielectric constant [82].

\[
V = \frac{C}{\epsilon_r^{1/2}} \quad (2.3)
\]

\[
\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (2.4)
\]

where \(V\) is the velocity in the medium (m/s); \(C\) is the velocity in free space (3\( \times \)10\(^8\) m/s); \(\epsilon\), \(\epsilon_r\) are the dielectric constant (Farad/meter) and the relative dielectric constant respectively; and \(\epsilon_0\) is the dielectric constant of air (8.85\( \times \)10\(^{-12}\) Farad/meter). The relative permittivity of concrete is typically between 5 and 12 depending primarily on the moisture content and signal frequency [83]. This gives velocities approximately between 87 and 134 m/s with the lower value relating to damp concrete [83].

Three major parameters, namely the center frequency, frequency bandwidth of the wave generated by the radar, and electromagnetic properties of concrete, influence the result of concrete thickness measurements with radar [84]. The use of signals with large bandwidth or high energy results in a high degree of range accuracy [85]. The range resolution that can be achieved by radar in concrete is [84]:

\[
\text{Equation (2.3)}
\]

\[
\text{Equation (2.4)}
\]
\[ \rho_r = \frac{c}{\sqrt{\varepsilon_r}} \frac{1}{2B} \]  

(2.5)

where \( \rho_r \), is the range resolution, \( c \) is the speed of light \((3 \times 10^8 \text{m/sec})\), \( \varepsilon_r \) is the dielectric constant of concrete, and \( B \) is the bandwidth of the wave. The detection capability of radar depends on the frequency bandwidth of an incident wave, while the penetration capability depends on the center frequency of the wideband incident wave [84]. Generally, as center frequency increases, frequency bandwidth also increases for a typical radar hardware system. This results in better detectability but reduced penetration capability. Greatest penetration is possible when the concrete is dry and the frequency low [83]. There is a tradeoff between achieving good detectability and penetration [83, 84].

2.2.3 Radiography

This involves the use of very short wavelength electromagnetic radiation, namely X-rays, gamma-rays or neutron rays, which are able to penetrate through solid media while being partially absorbed by the medium [86]. The amount of rays absorption depends on the density and thickness of the material through which the radiation is passing, and the characteristics of the radiation [86]. The radiation passing through the material is detected and monitored by electronic sensing equipment or viewed on a fluorescent screen/monitor. Radiography can be used to detect defects such as porosity, voids and inclusions having density that differs from that of the host material. The best performance is obtained when the defect is an appreciable thickness in a direction parallel to the radiation beam [86]. However, plain defects such as cracks are not always detectable and the ability to locate a crack will depend upon its orientation to the beam [86]. Any feature that causes a 2% or more change in absorption compared to the surrounding material will generally be detectable [86].

The major drawbacks to radiographic techniques include the health and safety issues associated with their use. X-rays systems use electrically powered linear accelerator to generate X-rays. Due to the electrical losses in concrete, much higher doses of X-rays are required to be effective, thereby leading to great safety concerns. On the other hand, gamma-rays use a nuclear source and require the nuclear probe to be brought into contact or into a hole drilled in the structure. Though potentially less dangerous than X-rays provided the nuclear source is carefully
controlled, the nuclear source imposes a lot of regulations and concern in its use and handling. Furthermore, because the gamma-ray procedure emits far less power than the X-ray system, the images tend to be weaker and require longer “stacking” time [86]. In neutron radiography, a neutron flux is passed through an object and is differentially attenuated by the various materials present in the object. The differential attenuation is then recorded on film as the flux emanates from the specimen to reveal details regarding the composition of the object [86]. Neutron radiography (NR) has been used with contrast agents to study internal cracking patterns in concrete [86-90].

Comparative studies have shown that the NR shows more cracking (Figure 2.10) than the X-ray radiograph [86, 90]. Pugliesi and Andrade [87] used digital neutron radiography (NR) technique to visualize cracks in concrete. They enhanced crack visualization by using samples impregnated with a high neutron absorbing substance (contrast agent) made from a chemical solution of gadolinium. Its neutron absorption microscopic cross-section is over 1000 times more than any element of the concrete composition [87]. They were able to obtain digital radiographs (Figure 2.10b) that gave better results, in terms of crack visualization, than those from digital X-ray radiographs (Figure 2.10c) and analog ones obtained by the NR technique of the same samples. The minimal discernible thickness of the gadolinium nitrate crystal deposits into the cracks obtained with the NR technique was about 0.6 µm. This is 25 times smaller than that obtained with conventional X-ray radiography [87]. However, NR cannot be easily used on large scale structures such as bridges [86].

![Figure 2.10](image)

Figure 2.10: (a) Conventional photograph of sample subjected to compressive strength to induce cracking, (b) digital neutron radiography of sample, (c) digital X-ray radiography [87].
2.2.4 Fiber Optic Sensors (FOS)

Fiber optic sensors have some unique properties which make them particularly suitable for defect monitoring in civil infrastructure [6]. Their flexibility makes them applicable on complex surfaces and difficult-to-reach areas. They are also capable of both local and distributive measurements (ranging from 1 mm to tens of kilometers) through multiplexing [91, 92]. Their small sizes (250-1000 μm) make them very suitable for embedding in civil infrastructure for in-situ monitoring. They are also immune to electric and magnetic interferences (EMI). In addition, they are able to measure a wide array of parameters including temperature, strain and loads acting on a structure. Finally, the use of fiber optics in telecommunication has helped in reducing the cost of fiber optic system components and has made them competitive with conventional sensors [92].

An optical fiber is a cylindrical dielectric waveguide made from silica glass or a polymer material. Both the core and the cladding are made from glass or plastic, and the surrounding coatings used to protect the optical fiber are made from acrylate or polyimide materials [16, 91]. The refractive index of the core is slightly higher than that of the cladding [93].

FOS are based on measuring changes in four main properties of the light passing through the optical fiber that can be modulated by various environmental perturbations [94, 95]. The properties are the phase, polarization state, intensity, and wavelength [95]. Based on these, FOS can be classified in to interferometric, polarimetric, intensity modulated, and spectrometric sensors respectively [95]. Table 2.2 summarizes the strengths and limitations of these four classes of FOS.

Three main approaches were identified in literature for fiber optic-based crack monitoring in concrete structures. The first involves detecting the fracture of the optical fibers; the second is by monitoring the amount of strain [96], while the third entails measuring the bending loss [49] of an embedded optical fiber or optical fiber array near an impact [54].
Table 2.2: Overview of the strengths and limitations of the four classes of fiber optic sensors [6, 91, 95, 97].

<table>
<thead>
<tr>
<th>FOS group</th>
<th>Operation principle</th>
<th>Benefits</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity modulated</td>
<td>Monitor changes in the intensity of the input light</td>
<td>Simplicity of implementation, low cost, possibility of being multiplexed, and ability to perform as real distributed sensors</td>
<td>Relative measurements only and variations in the intensity of the light source lead to false readings, unless a referencing system is used</td>
</tr>
<tr>
<td>Spectrometric</td>
<td>Monitor changes in the wavelength of the input light</td>
<td>Configuration, installation, and data processing are extremely easy; sensed information (shift in wavelength) is an absolute parameter; easy multiplexing; quasi-distributed point sensing; stable with age requiring no calibration</td>
<td>Not as sensitive as the interferometric sensors (about ±10 με); FBG manufacturing is capital intensive and requires highly skilled personnel; High sensitivity to temperature</td>
</tr>
<tr>
<td>Interferometric</td>
<td>Monitor changes or shifts in the phase of the input light</td>
<td>Sensed information (cavity length) is an absolute parameter; very precise (maximum resolution of ±0.01 με); low temperature sensitivity</td>
<td>Requires calibration each time readings are stopped; No multiplexing capability</td>
</tr>
<tr>
<td>Polarimetric</td>
<td>Monitor changes in the state of polarization of the lightwave as it travels along a single mode optical fiber</td>
<td></td>
<td>Requires polarization-maintaining optical fiber and polarization-insensitive couplers; requires long gage lengths for good strain resolution; limited applications because of the above requirements; difficult to manufacture</td>
</tr>
</tbody>
</table>

Although many different kinds of fiber optic crack sensors have been developed, most of them are limited in their applications [46]. Most are limited to indicating the existence of cracks only [98, 99]. Some FOS, especially point sensors, require prior knowledge of the exact crack locations, which cannot be easily predicted for concrete structures due to material inhomogeneity
Strain-based sensors are only able to detect the integral strain along their gauge length [95, 101]. However, if the selected gauge length is too large, it becomes very difficult to differentiate between one widely opened crack and many small harmless ones [46]. If the gauge length is small, many gauges are required to cover the plausible cracking region which makes it impractical [46]. The underlying principles of the three commonly used FOS techniques for crack detection are hereby described.

**Fabry-Perot (FP) Sensor**

There are two main types of FP sensor as illustrated Figure 2.11. In the extrinsic FP, a cavity is formed between the air–glass interfaces of two fiber end faces aligned inside a hollow-core tube (Figure 2.11a). The air gap between the mirrors defines the FP cavity while the distance separating the fuse spots is the gauge length [91]. In the intrinsic sensor, the cavity is formed between two partial mirrors formed as an integral part of a continuous length of fiber (Figure 2.11b) by fusion splicing an uncoated fiber to a fiber with a thin dielectric coating on the end [95]. The cavity is the sensing region. Strain variations induce changes in the length of the FP cavity, thereby inducing optical signals. During strain measurement, a white light is sent into one end of the fiber optic cable and the reflected signal is received by a readout unit. The strain in a FP sensor is measured using the following equations [91]:

\[
\varepsilon = \frac{\Delta L_{\text{cavity}}}{L_{\text{gauge}}} \tag{2.6}
\]

where \(\Delta L_{\text{cavity}}\) is the change in the cavity length and \(L_{\text{gauge}}\) is the gauge length. The real strain can be obtained by eliminating the temperature effect using the following equation:

\[
\varepsilon_r = \varepsilon - \beta \Delta T \tag{2.7}
\]

where \(\varepsilon\) is the total strain in a FP sensor obtained using Eq. (2.6), \(\varepsilon_r\) is the real strain of the structure, \(\beta\) is the thermal coefficient of structure, and \(\Delta T\) is the temperature change relative to the temperature at installation.
Figure 2.11: Extrinsic and intrinsic Fabry–Perot interferometric sensors: (a) Extrinsic sensor and (b) reflective and transmissive configurations of an intrinsic sensor [95].

**FBG Sensor**

The precise spacing of the grating, called the ‘pitch’, reflects the incident light with a narrow band centered about the ‘Bragg’ wavelength, defined by:

\[ \lambda_0 = 2n\Lambda \]  

(2.8)

where \( \lambda_0 \) is the Bragg wavelength, \( n \) is the average effective index of refraction of the grating, and \( \Lambda \) is the pitch spacing, as shown in Figure 2.12 [91]. The FBG also provides a linear response based on the measurement of wavelength shift (\( \Delta \lambda \)) due to the straining of the gauge [91]. The actual strain can be determined by taking into account the strain due to temperature by the equation:

\[ \Delta \lambda / \lambda_0 = (GF)\varepsilon + \beta\Delta T \]  

(2.9)

where \( \Delta \lambda = \lambda - \lambda_0 \), \( GF \) is the FBG gauge factor, typically about 0.75 – 0.82, \( \varepsilon \) is the strain, \( \beta \) is the thermal coefficient, and \( \Delta T \) is the temperature change relative to the temperature at installation.
In view of the above limitations in many FOS, Leung et al. [16, 46, 97] developed a novel distributed crack sensor that is able to detect cracks without a-priori knowledge of crack locations. The principle of the sensor is illustrated in Figure 2.13. When a crack opens in the concrete system, the optical fiber bends to maintain its continuity. This results in light loss from the fiber core to the surroundings. This causes the transmitted light in the fiber core and the backscattered optical signal to exhibit a sudden drop across the crack which is captured by the OTDR [46]. The exact location of the crack can be determined from the time corresponding to the signal loss (distance = time × light velocity in the waveguide) and the size of crack opening from the magnitude of the light loss [46].

This approach has a couple of drawbacks. The direction of crack formation needs to be known. It also requires several sensors to effectively capture all cracks. The weak backscattered power of the reflected light limits the dynamic range especially when using single mode optical fiber [46]. It also requires complicated measurement due to differential shrinkage of the concrete matrix around aggregate elements for the embedded case. In addition, performing conventional OTDR
on a straight fiber is not very effective because the cracking needs to almost reach the point of fracturing the fiber before the signal is attenuated enough to be detectable [49]. Because pulses of shorter than 10 ns duration are required in order to achieve spatial resolutions of within a meter, there is a conflict between short pulses for high resolution and more powerful ones for high signal to noise ratio required for proper signal assessment [49].

In another study, Kuang et al [102] developed an intensity based polymer optical fiber sensor for crack detection and vertical deflection monitoring in concrete beams. A segment of the POF cross sectional profile was removed to increase its sensitivity. This increases the amount of light loss in the fiber when bent because the cladding has been removed. This approach to sensitizing the fiber optic sensor (FOS) differs from others such as chemical tapering [103], intermittent etching [104, 105] and radial grooving [105] because the sensitized region of the sensor is limited to a segment of the POF and not the entire FOS cross-section. The benefits of this method include fast sensitizing procedure with the FOS produced having excellent sensitivity to bending/flexural loading and high level signal repeatability [106]. The sensor exhibited great potential for monitoring beam deflections during loading and detecting initial cracking and failure [102].
2.3 The Triboluminescence Phenomenon

The triboluminescence (TL) phenomenon has generated extensive research interest over the years because of its potential application for damage detection [24]. Triboluminescence also known as fracto- [107], piezo- [108], or mechano-luminescence [109], is the emission of light by solid materials when they are stressed or fractured [110, 111]. It has been estimated that about 50% of all crystal compounds exhibit a range of TL [112].

Although TL was reportedly discovered in the sixteenth century by Sir Francis Bacon, serious research into the phenomenon only began in the twentieth century. The main contribution of early nineteenth century research was the compilation of an extensive list of TL materials using highly subjective visual observation of the TL response as a function of time and quantity [112]. The development of the photomultiplier tube (PMT) in the 1930s and its application in triboluminescence studies in 1952 however introduced a quantitative technique for detecting, measuring, and comparing TL emissions objectively.

Recent research in triboluminescence includes those on [24, 25, 107-116]:

(i) Techniques to initiate the triboluminescent light emission with a known amount of mechanical energy, so as to investigate the relationship between mechanical energy input and the resulting TL emission intensity [117, 118].

(ii) Techniques to measure the TL emission spectrum [118, 119] with increased resolution and with a reduction in both the amount of triboluminescent material required and the time needed to obtain the spectrum.

(iii) The analysis of the spectral properties of the TL to understand the underlying mechanism of fracture-induced light emission [120, 121].

Light emission in a material can either be by incandescence or luminescence. Incandescence is light produced by heating an object to such a high temperature that the atoms become highly agitated leading to the glowing of the bulk matter [122]. It is an inefficient way of producing light as most of the energy is dissipated as heat. Incandescence is explained by Planck’s Black Body Emission theory. On the other hand, luminescence, sometimes referred to as “cold light”, is light produced at normal and lower temperatures. It involves an energy source elevating an electron of an atom out of its “ground” state into an “excited” state; and the sequential release
of energy in the form of light when the electron returns to its ground state [122]. It is a more efficient mechanism of light emission. Triboluminescence is a form of luminescence due to mechanical action or forces acting on a material. Triboluminescence may be divided into three types namely [21, 22] (1) elastico-, (2) plastico-, and (3) fracto-triboluminescence.

2.3.1 Elastico-triboluminescence

Elastico-TL is luminescence produced during the elastic deformation of solids, where neither fracture nor plastic deformation is required. This can be by mechanical or electrostatic interaction of dislocations with defect centers, or by thermal excitation in the stressed regions of solids [22]. Examples of crystals that exhibit elastic-TL include X- or g-irradiated alkali halides and ZnS:Mn [22].

Chandra et al. [23] provided experimental evidence supporting the suitability of a piezoelectrically stimulated electron detrapping model as being responsible for the elastic and plastic TL of ZnS:Mn. The suggested steps for elastic-TL in ZnS:Mn by the piezoelectric mechanism [23] are as follows: the deformation of ZnS:Mn crystals produces piezoelectric field because the crystal structure of ZnS is non-centrosymmetric [123]. The piezoelectric field results in decrease in the trap-depth, which causes the detrapping of electrons from filled-electron traps, with the electrons reaching the conduction band as illustrated in Figure 2.14.

![Figure 2.14: Schematic of elastico-TL in ZnS:Mn](image)

The electrons may recombine with the holes trapped in the defect centers or they may fall to the valence band with the energy being released non-radiatively. The energy released non-radiatively
may be transferred to the Mn$^{2+}$ ions to cause their excitation [124-127]. The de-excitation of excited Mn$^{2+}$ ions gives rise to the light emission characteristic of the Mn$^{2+}$ ions. Elastico-TL in ZnS:Mn starts at a pressure of about 1 MPa ($10^6$ Nm$^{-2}$) [128]. The piezoelectric charge density $\gamma$ generated at this pressure in the crystal with a piezoelectric constant ($d_{33} = 3.3 \times 10^{-11}$ C N$^{-1}$) [129] will be $3.3 \times 10^{-5}$ Cm$^{-2}$. This will result in an electric field $F$ given by the relation:

$$F = \frac{\gamma}{\varepsilon_o}$$

(2.10)

Given the permittivity $\varepsilon_o$ of the space is $8.85 \times 10^{-12}$ CNm$^{-2}$, an electric field of about $3.7 \times 10^6$ Vm$^{-1}$ or $3.7 \times 10^4$ Vcm$^{-1}$ will be developed near the crystal surface [128]. The internal electric field will however be about one order less than the external field on the crystal surface because the dielectric constant of ZnS crystals is 8.8 [128]. The piezoelectric field of the order of 3-10$^4$ Vcm$^{-1}$ is not adequate to cause electron detrapping from traps nor the impact excitation of Mn$^{2+}$ centers because an electric field of the order of 10$^6$ V cm$^{-1}$ is needed [128]. The local electric field near Mn$^{2+}$ ions may, however, be higher because of the local change in the crystals’ structure near Mn$^{2+}$ sites [114, 130]. This may result in a higher piezoelectric constant near the Mn$^{2+}$ sites [131, 132] to generate an electric field of the order of 10$^5$ Vcm$^{-1}$ that may cause sufficient decrease in the trap-depth but not sufficient to cause the impact excitation of Mn$^{2+}$ centers [128]. Subsequent electron–hole recombination may release energy non-radiatively for the excitation of Mn$^{2+}$ centers.

The theory of elastic-TL in ZnS:Mn nanoparticles is given by Chandra et al. [128]. Because ZnS is piezoelectric by nature, the TL of ZnS:Mn nanoparticles should be related to the conversion of mechanical energy into electrical energy, and then into light energy [128]. For thin films, the total number of photons emitted is directly related to the total electrostatic energy [133, 134]. When TL is induced by applying a load onto ZnS:Mn nanoparticles with the time constant $t_r$ for rise of pressure $P$ to the final pressure $P_o$ in time $t$, the peak TL intensity may be given as [128]:

$$I_m = \frac{\eta ad_o^2 p_o^2}{2}$$

(2.11)

where $d_o$ is the localized piezoelectric constant near the Mn$^{2+}$ centers in ZnS:Mn nanoparticles, $\eta$ is the efficiency for the radiative emission from Mn$^{2+}$ centers during the electron–hole
recombination, and $\alpha$ is a constant that is related to the density of the Mn$^{2+}$ centers and the density of electrons in shallow traps. Eq. (2.11) implies that the peak TL intensity will increase quadratically with $P_0$. At constant deformation rate, however, the peak intensity will increase linearly with the applied pressure:

$$I_m = \frac{\eta d_0^2 p_0}{2}$$  \hspace{1cm} (2.12)

When $\xi \gg \gamma$ (the rate constant for the relaxation of surface charges), the total TL intensity can be given as:

$$I_m = \int_{t_c}^{\infty} I dt = \eta d_0^2 p_0^2$$ \hspace{1cm} (2.13)

where $\xi = 1/\tau_r$ is the rate constant for the pressure rise, and is equivalent to the machine constant [128]. Since $d_0$, $\eta$, and $\alpha$ decrease with increasing temperature, it follows from Eqs. (2.11) and (2.13) that the peak and total TL intensity decrease significantly with increase in the temperature of the nano-crystals.

### 2.3.2 Plastico-triboluminescence

Plastico-TL is luminescence produced during plastic deformation of solids where fracture is not required. It can be excited by the mechanical or electrostatic interaction of dislocations with defect centers; electrification of crystal surfaces by the movement of charged dislocations; or thermal excitation in the stressed regions of solids such as colored alkali halides, II–VI compounds, alkaline-earth oxides, and metals [22]. Chandra et al. [135] reported on the luminescence arising from the plastic deformation of colored alkali halides using pressure steps. In the elastic region, the strain increases linearly with the stress, and the TL intensity also increased linearly with stress. In the plastic region, the strain and TL intensity also increased with stress according to the power law [135].

The steps involved in the TL of x- or $\gamma$-irradiated alkali halide crystals can be as follows and is illustrated in Figure 2.15: (i) Plastic deformation causes movement of dislocations, (ii) the moving dislocations capture electrons from the interacting F-centers lying in the expansion region of dislocations, (iii) the captured electrons from F-centers move with the dislocations and
they also drift along the axes of dislocations, and (iv) the recombination of dislocation-captured electrons with the holes lying in the dislocation donor band gives rise to the light-emission characteristic of the halide ions in hole centers [23].

Figure 2.15: Schematic energy level diagram of mechanoluminescence of coloured alkali halide crystals [135].

The TL intensity $I$ was found to be directly related to $\eta$, the efficiency of radiative electron–hole combination, and $n_d$, the number of electrons in the dislocation band at any time $t$ as follows:

$$I = \eta \beta n_d = \frac{\eta P_0^m \xi P_f r_f n_f}{K^m b \lambda (\xi - \phi)} \left[\exp(-\phi t) - \exp(-\xi t)\right]$$  \hspace{1cm} (2.14)

where $\beta = 1/\tau_d$, $\tau_d$ is the lifetime of electrons in the dislocations band, $P_0$ is the final value of pressure, $\xi = 1/t_r$, $t_r$ is the time-constant for rise of pressure, $K$ is referred to as the strength coefficient, $n$ is the work-hardening exponent, $m = 1/n$, $P_f$ is the probability of capture of interacting F-center electrons by the dislocations, $r_f$ is the radius of interaction between the moving dislocations and F-centers, $n_f$ is the density of F-centers in the crystals, $\phi = 1/t_p$, $t_p$ is the pinning time of the dislocations, $b$ is the Burgers vector, and $\lambda$ is the mean free path of the moving dislocations. The maximum TL intensity $I_m$ is given as:

$$I_m = \frac{P_0^m \xi P_f r_f n_f}{K^m b \lambda}$$  \hspace{1cm} (2.15)

The total intensity is given as
Both $I_m$ and $t_m$ increase according to the power law with an increase in the applied pressure. It has also been shown that the TL intensity depends on many parameters including strain rate, stress, density of F-centers, size of crystals, temperature, and luminescence efficiency [22, 112, 136-138].

2.3.3 Fracto-triboluminescence

Fracto-TL is luminescence produced due to the creation of new surfaces during the fracture of solids. During fracto-TL, there is creation of charged surfaces at fracture (Figure 2.16) due to processes such as piezoelectrification, movements of charged dislocations, and charged defect barodiffusion [22, 139]. There is neutralization of these surface charges by the charge carriers or ions produced from the dielectric breakdown of the intervening gases and solids. This results in the production of luminescence that resembles a gas discharge (e.g. sucrose, tartaric acid, and Rochelle salt) or luminescence of a solid (e.g. coumarin, resorcinol, and phenanthrene) or one that combines the characteristics of both the intervening gases and solids (e.g. uranyl nitrate hexahydrate, impure saccharin, and chlorotriphenyl-methane [22, 110].

![Figure 2:16 A schematic of the piezoelectric theory illustrating TL phenomena upon cleavage [139].](image)

If a crystal with thickness $H$ is cleaved along a plane parallel to its width $W$, with velocity of crack propagation being $v$, provided $a_3t < 1$, then the TL intensity may be given as [22]:

$$I = 2(\eta_1a_1 + \eta_2a_2)vwt$$ (2.17)
where $\gamma$ is the charge density of the newly created surfaces, $\alpha_1$ and $\alpha_2$ are the rate constants for the relaxation of charges on the newly created surfaces, $\alpha_3 = \alpha_1 + \alpha_2$, and $\eta_1$ is the luminescence efficiency associated with the movement of carriers produced by the dielectric breakdown of the crystals while $\eta_2$ is the efficiency associated with the movement of electrons and ions produced by the dielectric breakdown of intervening gases. According to Eqn 6, when a crystal is cleaved, initially the TL intensity should rise linearly with time $t$. At the end of cleavage (at $t = t_m, \nu = 0$), the TL intensity may be expressed as

$$l = [\eta_1 \alpha_1 + \eta_2 \alpha_2] Q_o \exp[-\alpha_3 (t - t_m)] \quad \text{(2.18)}$$

Where $Q_o$ is the surface charge at $t = t_m$. Eqn (2.18) shows the exponential decay of the TL intensity after the cleavage of the crystals. The time $t_m$ taken for cleaving the crystal of thickness $H$ is

$$t_m = H/\nu \quad \text{(2.19)}$$

From Eqn (2.19), the crack propagation velocity is

$$\nu = H/t_m \quad \text{(2.20)}$$

Based on Eqn (2.20), TL can be a tool for determining the velocity of crack propagation in crystals. The peak TL intensity at $t = t_m$ can be obtained from Eqn (2.17) and (2.19) as

$$l_m = 2(\eta_1 \alpha_1 + \eta_2 \alpha_2)\gamma WH \quad \text{(2.21)}$$

or

$$l_m = (\eta_1 \alpha_1 + \eta_2 \alpha_2)\gamma A \quad \text{(2.22)}$$

Since $A = 2WH$ is the area of the newly created surfaces. Eqn (2.22) implies that $l_m$ should increase linearly with $A$ and $\gamma$. The total intensity $I_T$ is given as

$$I_T = \int l \, dt = (\eta_1 \alpha_1 + \eta_2 \alpha_2)\gamma A/\alpha_3 \quad \text{(2.23)}$$

When $\alpha_1 = 0$, that is no gaseous discharge as is the case with ZnS:Mn, the emission will be primarily bulk TL and $\alpha_3 = \alpha_1$. When $\alpha_2 = 0$, that is, no bulk TL, emission is primarily by
gaseous discharge, and $\alpha_3 = \alpha_2$. Based on Eqn (2.23), the total TL intensity should be directly proportional to $A$, and crystals with higher values of $\gamma$ should have higher $I_T$. According to Eqns (2.22) and (2.23), $I_m$ and $I_T$ should decrease with increase in temperature because $\eta_1$, $\eta_2$, and $\gamma$ decrease with temperature increase. A specific temperature may however be reached above which $\gamma$ may decrease to the point that the breakdown of gases and solids becomes impossible, and TL no longer occurs [22].

2.4 Triboluminescent Sensor Systems

More recently, researchers have investigated the application of TL in damage detection [24, 111]. Triboluminescence-based sensor systems have the potential for wireless, in-situ, real time and distributed (WIRD) sensing that can enable continuous monitoring of civil and aerospace structures [21]. A TL-based sensor system comprising highly efficient triboluminescent materials could allow simple, real time monitoring of both the magnitude and location of damage with minimal parasitic influence to the host structure [114, 115]. They can be used as stress, fracture, and damage sensors [23, 140]. They have also been proposed for visualizing the stress field near the crack-tip, stress distribution in solids, and quasi-dynamic crack-propagation in solids [25, 26, 140-143]. In spite of all these research efforts, there is no information contained in the open literature that suggests commercial use of TL as a damage sensing mechanism [115]. Olawale et al [21] provides a detailed review of TL sensor systems.

2.4.1 Triboluminescent Materials for Sensing Applications

The principal requirements for any candidate triboluminescent material are that it should be highly efficient (allowing detection using inexpensive, compact detectors) and that it should emit light over a discrete and thus characteristic spectrum (allowing integration into an array of sensors to monitor damage location) [113, 114]. Bourhill et al. [144] used the photoluminescence (PL) quantum yield as a measure of the TL efficiency of different TL materials (Table 2.3) based on the assumption that both phenomena originate from the same excited state for the compounds studied. The ZnS–Mn has the highest triboluminescent efficiency among the TL materials investigated. Metal complexes are among the most intense TL materials known [114]. Metal complexes include europium tetrakis (dibenzoylmethide) triethylammonium [138][64], tris (1,3-di-tert-butyl-B-propane dione) terbium-p-dimethylamino pyridine [144] and dibromobis
(triphenylphosphine oxide) manganese [26, 121]. Most metal complexes contain a trivalent lanthanide as the emitting center [114].

Table 2.3: Solid-state photoluminescent quantum yields of a number of triboluminescent compounds [114, 144].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Europium tetrakis (dibenzoylmethide) triethylammonium</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>Europium tris (2-thenoyltrifluoroacetone)-phenanthroline</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>Hexakis(antipyrine) terbium triiodide</td>
<td>0.53</td>
</tr>
<tr>
<td>4</td>
<td>Tris(1,3-di-tert-butyl-β-propanedione) terbium-p-dimethylaminopyridine</td>
<td>0.71</td>
</tr>
<tr>
<td>5</td>
<td>Tris(1,3-di-tert-butyl-β-propanedione) samarium-p-dimethylaminopyridine</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>Tris(1,3-di-tert-butyl-β-propanedione) dysprosium-p-dimethylaminopyridine</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>Terbium trichloride hexahydrate</td>
<td>0.33</td>
</tr>
<tr>
<td>8</td>
<td>Mn:ZnS</td>
<td>1.00</td>
</tr>
<tr>
<td>9</td>
<td>Dibromobis(triphenylphosphine oxide) manganese</td>
<td>0.19</td>
</tr>
<tr>
<td>10</td>
<td>Europium (2+) hexacelsian</td>
<td>&gt;0.57</td>
</tr>
<tr>
<td>11</td>
<td>Samarium (2+ and 3+) hexacelsian</td>
<td>0.62</td>
</tr>
<tr>
<td>12</td>
<td>Cerium (3+) hexacelsian</td>
<td>0.44</td>
</tr>
<tr>
<td>13</td>
<td>Cholesteryl salicylate</td>
<td>0.13</td>
</tr>
<tr>
<td>14</td>
<td>N-Acetylanthranilic acid</td>
<td>&gt;0.28</td>
</tr>
<tr>
<td>15</td>
<td>Salicylsalicyclic acid</td>
<td>0.17</td>
</tr>
<tr>
<td>16</td>
<td>Menthyl-9-anthracenecarboxylate</td>
<td>&gt;0.43</td>
</tr>
</tbody>
</table>

In the study by Xu et al. [26], a comparison of the TL performance of different inorganic materials under identical mechanical stress conditions produced similar results for thin film and bulk materials (Table 2.4). Among the materials tested, the ZnS-based materials showed much higher TL intensities while the ZnS doped with Mn exhibited the highest luminous intensity of all the materials tested (Figure 2.17a). Furthermore, the study showed that a manganese doping
level of about 5% gives the highest TL response (Figure 2.17b). Based on the prevailing discussion, ZnS:Mn is a strong candidate for TL-based sensor systems.

Table 2.4: Triboluminescence of various materials [26].

<table>
<thead>
<tr>
<th>Group</th>
<th>Sample</th>
<th>TL intensity (cps)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal</td>
<td>ZnS</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>ZnS–Mn(_{0.05})</td>
<td>2800</td>
</tr>
<tr>
<td></td>
<td>ZnS–Cu(_{0.01})</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>Zn(_2)SiO(<em>4):Mn(</em>{0.01})</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>4</td>
</tr>
<tr>
<td>(\text{X}_2\text{O}_3) (X = Al or Y)</td>
<td>(\alpha)-Al(_2)O(_3)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(\alpha)-Al(_2)O(<em>3):Mn(</em>{0.01})</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>(\text{Y}_2)O(_3)</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(\text{Y}_2)O(_3):Eu</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>MgAl(_2)O(_4)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>CaAl(_2)O(_4)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>SrAl(_2)O(_4)</td>
<td>36</td>
</tr>
<tr>
<td>Fluorite</td>
<td>ZrO(_2)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>HfO(_2)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>CeO(_2)</td>
<td>3</td>
</tr>
<tr>
<td>Perovskite</td>
<td>YBa(_2)Cu(_4)O(_8)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>PbZr(<em>{0.52})Ti(</em>{0.48})O(_3)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Pb(<em>{0.93})La(</em>{0.07})Zr(<em>{0.60})Ti(</em>{0.40})O(_3)</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\)TL intensity was measured as a function of friction applied to the material by a brass rod of 1 mm diameter under a load of 5 N and slide speed of 6.3 cm/s (2.5 rps).
2.4.2 Artificial Skin to Sense Mechanical Stress

Xu et al. [26] successfully developed an artificial skin made from a self-diagnosis piezoelectric thin film that can reproducibly emit strong visible light when stressed. Such a system can detect and analyze the stress on dynamic structures without the use of an electrode or any physical contact. A major finding of Xu et al. [26] is the reproducibility of the TL of ZnS:Mn. Figure 2.18a shows that the response curve of the luminescence intensity of ZnS:Mn to friction is reproducible. Reproducibility was also observed when the skin was subjected to compression (Figure 2.18b) and impact loads (Figure 2.18c). In Figure 2.18b, two luminescent pulses (I and I') corresponding to the increase and release of stress, respectively, were generated during one cycle of applied stress, all of which were reproducible as shown in II and II’. The total numbers of the emitted photons of each pulse were comparable.
Figure 2.18: (a) Luminescence intensity response of the ZnS:Mn film to the friction, (b) response to compression stress of 500 N, applied at a cross head speed of 0.1 mm/min, and (c) response to impact stress applied by a free-falling steel ball [145].

These results differ substantially from those of other reported piezoluminescent materials like gamma-colored alkali halide crystals and rubber in which the emitted photons normally decreased greatly during repeated cycles of stress [145]. Figure 2.18 (c) shows the single optical pulse obtained in response to mechanical impact. The energy conversion efficiency for converting mechanical energy to photon energy was found to be of the order of $10^{-2}$ and $10^{-6}$ for compression and impact cases, respectively, values similar to those reported for piezoelectrics [145]. The luminescent intensity also increased with increasing mechanical stress (Figure 2.19 (a) and (b)). The TL intensity from the thin film was more than one magnitude higher than that obtained from the bulk material synthesized in the same way. The significant improvement is attributed to the high orientation and crystallization of the film and the nano sized grains. The TL of ZnS:Mn is from the Mn emitting center due to the transition of $^4T_1$ to $^6A_1$ [146].

Figure 2.19: (a) Dependence of the luminescence intensity on load in the case of friction and (b) dependence of the luminescence intensity on the falling height of a steel ball on impact [145].
In a related work, Xu et al. [147] developed a similar stress sensing system that enables a direct view of stress distribution by using SrAl$_2$O$_4$:Eu. They found that SrAl$_2$O$_4$ doped with 0.5 mol% Eu by wet process from Eu(NO$_3$)$_3$.2H$_2$O gives the strongest TL intensity, which was an order of three magnitudes higher than that of the well-known TL material of quartz [108]. The photoluminescence (PL) and TL spectra from SrAl$_2$O$_4$:Eu is characterized by broadband emission with a peak wavelength of nearly 520 nm for both PL and TL. This implies that both TL and PL were emitted from the same emission center of Eu ions due to the transition of the Eu ions between 4f$^7$ and 4f$^6$5d$^1$ [147-149]. The stressed sample emitted intense visible green light from its two ends. This approach has a benefit over thermography in that it is not limited to evaluating stress distribution under fatigue alone [147, 149]. The TL decreased with repetitive loading, similar to other TL materials such as colored alkali halides [150, 151]. The TL intensity, however, recovered completely after being irradiated by an UV light (365 nm) at room temperature, indicative of luminescence by a nondestructive deformation of SrAl$_2$O$_4$:Eu [147].

2.4.3 Impact Sensors

Low Impact Sensor (<10 m/s)

Womack et al. [24] carried out a study targeted at quantifying the relationship between TL intensity and impact energy of ZnS:Mn under low impact velocity of less than or equal to 10m/s [152]. Figure 2.20 gives a typical emission spectrum for the ZnS:Mn irradiated with a xenon lamp at a wavelength of 355 nm. The ZnS:Mn emits bright yellow light when excited with a broad emission peak centered at 585 nm and a full width at half maximum (FWHM) of about 125 nm. Hollerman et al (2008) [152] also reported the same excitation emission peak for ZnS:Mn as Womack et al (2004) [24] but a different full width at half maximum (FWHM) of 65 nm. The ZnS:Mn crystals were impacted directly with a steel ball falling under gravity in a custom-built impact test rig with increasing impact energy.
This study indicates that only a few crystals of ZnS:Mn is required to achieve a significant light output during impact, and that the TL decay follow the standard exponential decay curve of luminescence under phosphor thermometry. Figure 2.21 shows the variation in TL emission from the ZnS:Mn crystals as indicated by the output voltage from the photomultiplier tube (PMT) as a function of the drop height. Two regions of interests can be observed. In the first region, threshold energy of approximately $1.6 \times 10^{-2}$ J was observed to be the minimum energy required by the projectile to fracture the TL crystals and emit light. The intensity then increased rapidly with increased projectile kinetic energy up to about 0.26 J.

The second stage starts at 0.26 J with a shallow slope indicating that the sample has become less sensitive to impact energy. At this stage, it was proposed that the projectile was already cracking as many crystals as it could in the impact area so the increased energy levels could not generate higher TL responses. Impact velocities greater than 0.5 m/s were found to produce measurable TL light [24]. Earlier work done in applying triboluminescence as low impact sensor can be found in Ref. [140].
Figure 2.21: Plot of the peak TL intensity as a function of impact kinetic energy for the ZnS:Mn powder [24].

*Meso-velocity Impact (100 m/s–1 km/s)*

Hollerman et al. [152] used fluorescent decay time of ZnS:Mn to detect TL from lab-generated impacts. The fluorescence decay time is unique to each material and can be defined as the time needed to reduce the light intensity to $e^{-1}$ (36.8%) of its original value [152]. The reduction in light intensity from the cessation of excitation is a simple decaying exponential for many luminescent materials [24, 111, 153] and is given by the relation [154]:

$$I = I_0 \exp\left(\frac{-t}{\tau}\right)$$  \hspace{1cm} (2.24)

ZnS:Mn is strongly triboluminescent with a prompt fluorescence decay time of about 300 μs [111, 152]. The study used projectiles at meso-velocities to mimic impacts caused by secondary debris produced when meteoroids hit the Moon. The goal was to distinguish between the light from TL and the light from other sources such as impact flash. It was concluded that TL can be produced during meso-velocity impacts of about 400 m/s and that it may be difficult to separate TL from the other light sources, such as debris impact, sparks, or flashes caused by thermal effects or phase changes. This is because TL is sometimes not intense enough to overcome the other time dependent sources [152].
**Hypervelocity Impact (41 km/s)**

The application of TL sensors to detect hypervelocity impacts was fueled by the loss of the Columbia orbiter [111]. The research started in August 2003 at the NASA Marshall Space Flight Center (MSFC) in Huntsville, Alabama. The study involved shooting 1 mm aluminum spheres at hyper velocity (5–6 km/s) on to aluminum plate targets coated with ZnS:Mn and binder paint. Poly (phenyl methyl) siloxane (PPMS) gave the toughest and most wear resistant paint and was sufficiently resistant to hypervelocity impacts [24]. A combination of ZnS:Mn and PPMS 1:4 ratio by weight was consequently used. The test result (Figure 2.22) shows that there is a rapid but late increase in TL signal from the ZnS:Mn when impacted as against the gradual and earlier increase in the light from the flash of the gun as measured by the unshielded detector [111]. This indicates that hyper velocity impact can be detected by a TL sensor system [111].

![Figure 2.22](image-url)  
*Figure 2.22: Light intensity comparison from unshielded and shielded detectors as a result of a hypervelocity impact on a ZnS:Mn coated plate [111].*
2.4.4 TL Signal Detection and Transmission in Composites

The utilization of TL materials as sensors in composite materials necessitates the ability for transmitting the emitted signals. Most of the works in open literature involve end and/or side coupling of light through optical fibers to transmit emitted light from damage zones in composites [25, 114]. This is, however, inefficient, resulting in a very poor signal to noise ratio [25]. Furthermore, the integrity of the sensor system is compromised when the optical fiber is fractured. To overcome these limitations, Sage et al. [25] used a combination of polymeric optical fiber having its core doped with a highly photoluminescent material and triboluminescent damage sensors. When fracture occurs, the TL signal from the embedded TL sensor is efficiently absorbed by the photoluminescent material and re-emitted as light, which can match the waveguide modes of the polymeric fiber. This was achieved by using materials with significant spectral overlap between the TL emission and the absorption profile of the photoluminescent material (Figure 2.23).

Hollow silica capillaries with an inside diameter of 100 mm and an outside diameter of 170 mm were vacuum-filled with a benzyl alcohol solution of the highly efficient photoluminescent material, rhodamine 6G [155]. The refractive index of the benzyl alcohol core (n = 1.539 at 633 nm) was larger than that of silica, consistent with wave guiding [25]. In addition, the TL
emission spectrum of the triboluminescent material tris (1,3-di-t-butyl-bpropanedione) terbium-
p-dimethylaminopyridine significantly overlapped the absorption spectrum of rhodamine 6G
(Figure 2.23). While the peak of the terbium triboluminescence occurred at 548 nm, the peak
absorption and emission of rhodamine 6G occurred at 537 nm and 565, respectively.

The sensor system was incorporated into TL terbium complexrich resin and carbon fiber
reinforced polymer (CFRP). Both were then tested by impact loading. The TL responses
obtained is as shown in Figure 2.24. The S/N ratio achieved was orders of magnitude greater
than that achieved with a conventional silica fiber (Figure 2.24 (a) and (b)), even in black CFRP
panels (Figure 2.24 (b) and (c)) [25]. The system acted as a truly global damage sensor in resin
or glass fiber reinforced polymer (GFRP) while in CFRP, it acted as a local damage sensor
because it could only detect signal close to the optical fiber [25].

Figure 2.24: (a) The optical damage signal upon impacting a resin, (b) a CFRP panel containing
a silica photoluminescent fibre and (C) CFRP panel post-impact [25].
2.5 Summary

Virtually all the work done on the application of TL for damage sensing are based on impact damage. The review done on damages in concrete structures clearly indicates that damage in such structures are not limited to impact damage. There is therefore a need to investigate the suitability of TL for damage sensing under flexural and fatigue loading before it can be considered suitable for CSHM. Another important observation is that most work done on TL damage sensing have focused on polymer matrices as the host structure. Concrete structures however, have very different microstructure and properties from polymer systems. Hence, it is imperative to investigate the TL performance of ZnS:Mn in a concrete system.
CHAPTER THREE

DAMAGE MONITORING IN CEMENTITIOUS COMPOSITES
BY DIRECT DISPERSION OF ZNS:MN

The first approach investigated in developing a cementitious composite system with a
triboluminescence-based damage detection system involved the direct dispersion of ZnS:Mn
crystals in a mortar system. The hypothesis is that as the system is loaded and crack formation
occurs, the stress field developed around and along the crack path will cause the excitation of the
crystals along the crack path. Such a system will exhibit ubiquitous damage detection. It will be
able to detect any crack provided there is a TL crystal along the crack’s path. To have an
effective system, there is the need to determine the concentration level of the ZnS:Mn crystals
required to ensure that any crack at any point in the system is detected without adversely
affecting the mechanical properties of the cementitious composite.

3.1 Experimental

The experimental procedures are as described in the following sections.

3.1.1 Sample Preparation

The cementitious optical sensor was prepared by physically mixing fly ash, water, cement, and
ZnS:Mn crystals. The various properties of the constituents are given in Table 1. The ZnS:Mn
was purchased from Phosphor Technology, UK. The thoroughly blended mixture was cured by
adding water, and the resulting paste poured into a mold. The samples were then allowed to cure
for predetermined number of days. The prepared molds had two plastic optical fibers already
attached within, to allow for their embedment in the cured cementitious patch. The fibers pick up
the triboluminescence signals emitted as the material is loaded, thereby indicating levels of
internal damage. While the cement acts as the binder, the fly ash helps in improving the patch’s
properties by enhancing strength development, reducing voids and negating the effect of
shrinkage. The ZnS:Mn is the triboluminescence material that emits light when stressed or
fractured. The samples produced had dimensions 50 x 50 x 6.25mm (2 x 2 x 0.25inch).
Table 3.1: Main constituents of the TL cementitious optical sensor.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bulk specific gravity</th>
<th>Particle size distribution (μm)</th>
<th>Proportion (by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I/II Portland cement</td>
<td>3.15</td>
<td>1-50</td>
<td></td>
</tr>
<tr>
<td>Boral class F fly ash</td>
<td>3.00</td>
<td>25</td>
<td>25% of cement</td>
</tr>
<tr>
<td>ZnS:Mn</td>
<td>4.10</td>
<td>5-20</td>
<td>0,5,7.5,10,15,20,25% of cementitious mixture</td>
</tr>
<tr>
<td>Water</td>
<td>1.00</td>
<td></td>
<td>Approx. 50% of cement</td>
</tr>
</tbody>
</table>

3.1.2 Mechanical Tests

The impact samples were loaded in a custom-built impact rig (Figure 3.1) where they were impacted with a pneumatically-controlled piston at specific pressure values. The rig was fed by a compressed air line, and controlled with an adjustable pressure and release valve.

![Figure 3.1](image-url)

Figure 3.1: Schematic of the custom-built impact rig for assessing TL performance of sensor patch samples.

The compressive strength of samples were determined using a CM-3000-DB compression rig from Test Mark Industries (Figure 3.2) according to ASTM C109/C109M – 08 standard test methods for compressive strength of hydraulic cement mortars, using cube specimens of size 50mm (2inch.). The operation of the impact rig and PMT was controlled using a MatLAB graphical user interface with a NI USB-6210 data acquisition device from National Instruments.
3.1.3 Triboluminescent Signal Measurement

The triboluminescent intensity was measured by connecting the plastic optical fibers (POF) from the cured POF to the PMT which converted it into an electrical signal (voltage). A National Instrument data acquisition device linked the PMT to a personal computer for real-time data collection. Figure 3.3 provides an overview of the experimental setup for assessing the triboluminescent performance of the cementitious sensor patches.

Figure 3.3: Block diagram of impact test setup for TL performance assessment of cementitious sensor patches.
3.2 Results and Discussion

The results from the studies are hereby presented and discussed.

3.2.1 Effect of ZnS:Mn Concentration on Triboluminescent Response

Figure 3.4 shows a sample of the triboluminescence response obtained during the impact tests. The pulse and subsequent decay of the triboluminescence emission observed is characteristic of the ZnS:Mn decay profile, and is comparable to those obtained in literature from similar tests using the same triboluminescence material (ZnS:Mn) [156]. The wavelength of the ZnS:Mn, according to the manufacturer (Phosphor Technology, UK), is 585 nm. The color of the emission observed from tests using the ZnS:Mn is orange–yellow. The observed TL profile from the fabricated cementitious optical sensor indicates that the dispersed ZnS:Mn crystals retain their triboluminescent property within the high-alkaline environment of the mortar.

![Figure 3.4](image)

Figure 3.4: Typical TL response obtained (a) during the impact tests.

Figure 3.5 shows the triboluminescence responses obtained from the TLCOS samples containing different concentration levels (percentage by weight) of the triboluminescent material (ZnS:Mn). Five samples were tested at each concentration level under same loading condition. Overall, there tends to be an increase in the triboluminescence response of the samples with increasing
ZnS:Mn concentration levels. Triboluminescence signals were obtained at concentration levels as low as 2.5 and 5%. However, not all the samples tested at these low concentration levels yielded a triboluminescence response on impact. Triboluminescence responses were obtained for all five samples tested at concentration levels of 7.5% and higher. The absence of triboluminescent response from some of the samples with low concentration levels was due to insufficient ZnS:Mn particles in the patch. As a result, the crack path may miss the scantily dispersed ZnS:Mn crystals. Consequently, a ZnS:Mn percolation level of 7.5% is required for an effective TLCOS.

A significant jump in the mean triboluminescent response was noted between 5% and 7.5% concentration levels. The mean triboluminescence signal quadrupled from about 0.04V at 5% concentration level to about 0.16V at 7.5% concentration level. This level of triboluminescent response was maintained with slight variations up to the 20% concentration level. At concentration levels of 7.5% weight and above, there are more ZnS:Mn crystals dispersed within the composite system that are being activated by the impact energy during testing. These higher levels of ZnS:Mn concentration also make it possible for sufficient number of crystals to be
located near to the transmission component (polymer optical fiber) of the TLCOS. The effect of the opaque cementitious particles of the cementitious component of the composite kept the amount of TL signal successfully coupled into the POF fairly constant for all ZnS:Mn concentration levels of 7.5-20%. A significant increase in the triboluminescent response was however observed when the concentration level reached 25%. The mean triboluminescent signal increased by about 2.5 times from about 0.16V at 7.5% concentration level to a value of 0.42 V at 25% concentration level. At this level, there were much more crystals in the composite and around the POF to reduce the effect of the opaque cementitious component and cause a significantly higher TL signal generation and coupling.

### 3.2.2 Influence of ZnS:Mn Concentration on Strength of Cementitious Patch

This work investigated the effect of ZnS:Mn concentration levels on the strength of the cementitious patch, by testing to failure, five cube samples of (50.8 x 50.8 x 50.8 mm) at each concentration level investigated. The particle size distribution (PSD) of the ZnS:Mn used ranged from 5–20 μm while that of the unhydrated cement particles ranged from 1–50 μm [30]. Figure 3.6 shows the effect of ZnS:Mn concentration levels on the compressive strengths of 28 days cured samples.

![Figure 3.6: Effect of ZnS:Mn concentration levels on the compressive strengths of 28 days cured samples.](image)
days-cured samples. The result shows that there was a reduction in the compressive strength of the pristine cementitious patch from about 29.5 MPa to about 26 MPa at ZnS:Mn concentrations of 5 and 7.5%. Enhancement of the compressive strength was however observed at ZnS:Mn concentration levels of 10 and 15% with mean values of about 31 and 30 MPa, respectively compared to a mean value of about 29 MPa for the mortar system with no ZnS:Mn content. The triboluminescent crystals seem to provide some form of particle reinforcement at these concentration levels. Although degradation in the compressive strength was observed at 20% triboluminescent crystal concentration, the value (28 MPa) was still greater than those at 5 and 7.5% concentration levels. There was however a drastic loss of strength at a ZnS:Mn concentration of 25%. This represents a reduction of about 29.31% when compared to the control.

About 100MPa is required for the cleavage of a ZnS:Mn particle [22, 128] while the maximum value of the compressive strength obtained for the samples tested was about 32 MPa. This implies that the products from the curing of cement (cement hydration) are the weaker link in the TLCOS system and ZnS:Mn has the potential to act as particulate reinforcement in the system. It is very likely however that sample fabrication process may have caused the coagulation of the crystals that may introduce more microvoids that make the TLCOS system weaker. The SEM characterization will help in gaining a better understanding of this.

### 3.2.3 SEM Characterization

The microstructure of the samples was characterized using the backscattered mode of the Field Emission Scanning Electron Microscope (JOEL JSM-7401F). The images are as shown in Figure 3.7. The SEM micrograph of the 28 days-cured samples with 0% wt ZnS:Mn (Figure 3.7(a)) has little or no ettringites unlike the 28 days cured sample with 25% wt ZnS:Mn (Figure 3.7(b)). It may be concluded that at this high ZnS:Mn concentration level of 25%, the crystal content may affect the hydration process by slowing down the conversion of the needle-shaped crystals of calcium sulfoaluminate hydrate (ettringites) into the monosulfate hydrate with hexagonal plate morphology.
Figure 3.7: SEM micrographs of 28-days cured cementitious composite (a) 0% ZnS:Mn by wt, (b) 25% ZnS:Mn by wt.

The monosulfate hydrate makes concrete vulnerable to sulfate attack. The same behavior was observed in samples cured for a shorter period (10 days) and with lower ZnS:Mn (5% wt) concentration (Figure 3.8).

Figure 3.8 SEM micrographs of 10-days cured Cementitious composite (a) 0% ZnS:Mn by wt, (b) 5% ZnS:Mn by wt.

3.2.4 EDX Analysis

Energy dispersive X-ray spectroscopy analysis (EDX) was carried out to help in identifying the ZnS:Mn in the TLCOS. Figure 3.9 shows a sample (5% wt ZnS:Mn, 10 days cure) with no traces of ZnS:Mn while Figure 3.10 shows another portion of the same sample with a significant level of ZnS:Mn present. These observations support the scarcity effect assumption that at this low
concentration level of the ZnS:Mn, the crystals may be so widely spaced that cracks and deformations elude them and fail to effectively excite them. This is the reason why two of the five TLCOS samples with low ZnS:Mn concentration levels (2.5 and 5%) failed to produce triboluminescent responses on impact.

Figure 3.9: EDX result of Sample (5% wt ZnS:Mn, 10 days cure) with no ZnS:Mn presence at location under examination.

Figure 3.10: EDX result of Sample (5% wt ZnS:Mn, 10 days cure) with ZnS:Mn present.

Figure 3.11 clearly shows the ZnS:Mn in the cementitious composites. Crystals of ZnS:Mn require about 1MPa (10^6Nm^-2) for elastico-triboluminescence to commence with an elastic limit of about 30MPa (30 x 10^6Nm^-2), while about 100MPa (1 x 10^8Nm^-2) is required for fracto-triboluminescence [15,16]. About 6% of the triboluminescence occurs during elastic
deformation, 14% at fracture, while 80% occurs during plastic deformation [157]. Since the compressive strength of the sample is about 40 MPa, it may be suggested that the observed crystals in Figures 3.11 and 3.12 did not fracture extensively during the test. However, one of the crystals shows fracture lines on its surface. Moreover, there tends to be coagulation of the crystals within the cementitious composite system. It may be possible to reduce the TL crystals requirement of the system by improving the dispersion of the coagulated crystals throughout the composite system. This will also help to reduce any negative effect the presence of the TL crystals may have on the structural properties of the cementitious composites.

Figure 3.11: EDX result of Sample (5% wt ZnS:Mn, 10 days cure) with ZnS:Mn clearly identified.

Figure 3.12: SEM micrograph showing the interface between ZnS:Mn crystals and the products of hydration (5% wt ZnS:Mn, 10 days cure): A- ettringite, B-flyash, C-ZnS:Mn, D-calcium silicate hydrate, E-calcium hydroxide.
3.3 Summary

This work has demonstrated the feasibility of utilizing a triboluminescence-based cementitious optical sensor for monitoring and detecting internal damage in concrete infrastructural systems. The ZnS:Mn crystals retained and exhibited their TL property in the high alakine cementitious composite systems studied. A ZnS:Mn percolation level of 7.5% weight percent will ensure that there is sufficient triboluminescent crystals in the system for damage to be well captured. Based on this study, it was demonstrated that a ZnS:Mn concentration level of sensor 10–15% gave high triboluminescent response without compromising the strength of the triboluminescence-based cementitious optical sensor system. The importance of proper sample preparation method has been highlighted. This is critical in getting good dispersion of the ZnS:Mn crystals in the matrix and in reducing microvoids that may adversely affect the strength of the system.
CHAPTER FOUR

BIO-INSPIRED *IN-SITU* TRIBOLUMINESCENT OPTICAL FIBER SENSOR

A major challenge militating against triboluminescence-based sensing systems has to do with the effective capture and transmission of the optical signal generated within opaque composites like concrete and carbon fiber reinforced polymer. The common approach is to incorporate the crystals into the resin and infuse into the fiber layup in which optical fiber has been placed. The whole part is then cured. There are however many limitations with this approach.

Firstly, the concentration level (weight fraction) of the triboluminescent (TL) crystals in the host matrix required for good TL response is usually high. This introduces parasitic weight effect which is highly undesirable. The density differences between the TL crystals and resin matrix may also cause the settling of the crystals during curing. There will therefore be uneven dispersion of the crystals in the cured composite part or structure. Another problem associated with this approach is filtration during the infusion process. The second approach is to incorporate the crystals in polymer and produce as thin films. This approach is however limited to surface mounting on structures. There is also the problem of incorporating the signal transmission component. If the thin film is placed within a laminate, the risk of delamination increases.

The *in-situ* triboluminescent optical fiber (ITOF) sensor overcomes most of these challenges. The (ITOF) sensor mimics the sensory receptor of the human nervous system (HNS) by converting the energy from damaging events like impact and fracture into optical signals that are indicative of the magnitude of damage. The ITOF sensor has the potential for wireless, *in-situ*, real time and distributed (WIRD) sensing. Furthermore, it eliminates the problems associated with parasitic weight and filtration during composite fabrication. The ITOF sensor combines the highly desirable properties of optical fibers such as lightweight, small size, immunity to electromagnetic interference and capacity for distributed sensing [18, 19], with the triboluminescent property of ZnS:Mn.
Before the new sensor can be incorporated into composite parts for damage detection and monitoring however, key design factors affecting its performance have to be identified and the appropriate levels that give enhanced TL response need to be determined. The work in developing a viable production methodology and for characterizing the ITOF sensor is hereby reported. In the proof of concept experiments, four factors were investigated namely: presence or absence of cladding on the polymer optical fiber, ZnS:Mn/epoxy ratio, crystal size, and coating thickness. Based on these results, a second set of experiments was conducted with an improved fabrication methodology for the ITOF sensor.

4.1 Operating Principle of the ITOF Sensor

The ITOF sensor (Figure 4.1) consists of a polymer optical fiber (POF) with a highly sensitized section, the triboluminescent sensory receptor (TSR). The TSR is made by mechanically removing the jacket in that section along the length of the POF, and coating with fast curing epoxy containing dispersed ZnS:Mn crystals which is one of the most efficient triboluminescent materials known [144]. The ITOF sensor senses damage in the composite structure by converting the mechanical energy of the damage causing event like impacts and crack propagation into triboluminescent (TL) optical signals. The TL signals are then transmitted through the POF to a photodetector such as a photomultiplier tube (PMT) or a photodiode. The photodetector converts the TL optical signals into electrical signals that can be analyzed by a computer system for damage characterization (Figure 4.2).

Figure 4.1: A schematic of the ITOF sensor.
Figure 4.2: An ITOF based sensing system for SHM of bridges a) damage-sensitive region with ITOF sensor, b) TL (damage) signal from ITOF sensor due to crack, c) signal transmission by ITOF sensor and signal detection by PMT, d) signal analysis and damage identification.

The operation of the ITOF sensor is analogous to that of the sensory receptors in the human nervous system that are able to convert the energy of the stimuli into nerve impulses that can be transmitted through the neurons. The sensitized section of the ITOF acts like the sensory receptor of the HNS while the optical fiber acts like the neuron for transmitting the TL optical signal to the photodetectors.

4.2 Sensor Characterization Tools
Impact tests were carried out using a custom-built impact rig (Figure 4.3). The impact energy was defined based on Newton’s equations for a free-falling body with the assumption that the air resistance is negligible and the impacting mass does not touch the side of the aluminum drop tube.
A detailed description of the custom-built impact rig can be found in [27]. The TL signals picked by the optical fiber are transmitted to the Hamamatsu Corporation (H5784-01) photomultiplier tube (PMT), where they are converted into electrical signals (voltage) and quantified. The PMT was powered with 0.5 V from an Agilent E360A triple output DC power supply. A custom-written program based on Matlab was used to control the operation of the PMT and to display the TL response values and profiles through a National instrument NI-USB-6210 data acquisition device. Analysis of variance (ANOVA) was used to analyze the result using Minitab statistical software.

Microscopic study was conducted using Field Emission Scanning Electron Microscope (JEOL JSM-7401F) to gain insight into the interface between the POF and the ITOF coating. Dynamic mechanical analysis (DMA) characterization was carried out with a Q800-0918 (TA Instruments). For this characterization, thin films of the epoxy containing 25% and 50% by weight of ZnS:Mn were fabricated using a press at room temperature. These are representative of the ITOF coatings used in this study. The films produced have a thickness of about 0.3mm and were cut into samples of 20 x 3 mm using the Laser cutter ML300. In order to determine the storage modulus and Tg, temperature ramp/frequency sweep was performed on the samples at a frequency of 1 Hz and at 3°C/min. The data from the tests were analyzed using Universal Analysis 2000.
4.3 Design Parameters Evaluation with Sensors Fabricated with Dip Process

Figure 4.4 gives an overview of the dip process for the fabrication of the ITOF sensor. The ITOF sensor fabricated consisted of a 1 mm diameter polymer optical fiber (POF) produced by Mitsubishi Rayon Company (SH-2001-J), a portion of which the jacket had been removed to expose the desired length. The properties of the POF are as shown in Table 4.1.

Table 4.1: Specification of the ESKA CK40 polymer optical fiber (POF).

<table>
<thead>
<tr>
<th></th>
<th>Core</th>
<th>Clad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>PMMA resin</td>
<td>Fluorinated polymer</td>
</tr>
<tr>
<td>Diameter (typical)</td>
<td>980 µm</td>
<td>1000 µm</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>3.09 GPa</td>
<td>0.68 GPa</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.492</td>
<td>1.405</td>
</tr>
<tr>
<td>Yield strength</td>
<td>82 MPa</td>
<td></td>
</tr>
<tr>
<td>Transmission loss (at 650 nm)</td>
<td>200dB/km</td>
<td></td>
</tr>
<tr>
<td>Maximum operating</td>
<td>70°C</td>
<td></td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approximate weight</td>
<td>1 g/m</td>
<td></td>
</tr>
</tbody>
</table>

The appropriate weight of ZnS:Mn (Supplied by Phosphor Technology, UK) and fast cured epoxy (Devcon 5 Minute Epoxy, #14250) required to get the desired concentration ratio was measured, mixed and stirred manually to ensure good dispersion of the crystals in the epoxy matrix. The coating of the exposed portion of the POF was accomplished by the dip process. The dipping had to be done immediately the ZnS:Mn and fast cure epoxy were mixed. The system was then allowed to cure. The ITOF sensors produced for this study had a total length of 640mm with a sensitized region of 40mm.
4.3.1 Test Procedure
In the first phase of this characterization, design of experiments was used to investigate four factors that were thought to affect the performance of the ITOF sensor. These factors are the presence or absence of cladding on the POF, ZnS:Mn/epoxy ratio, crystal size, and coating thickness. Table 4.2 gives the different levels of the four factors investigated in this study. The two-level full factorial design resulted in 16 sensors being produced and randomly tested.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Low level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS:Mn-Epoxy concentration (by mass)</td>
<td>1:1</td>
<td>1:3</td>
</tr>
<tr>
<td>ZnS:Mn average crystal size (µm)</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>Presence of cladding</td>
<td>Cladded</td>
<td>Uncladded</td>
</tr>
<tr>
<td>Coating thickness (mm)</td>
<td>0.66</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The ITOF sensors’ coating thickness at the low level ranged from 0.55 to 0.82 mm, while the value ranged from 1.15 to 1.73 mm at the high level. The average values for the samples are given in Table 4.2. The samples were then impacted with a small mass of 33g at five monotonically increasing impact levels namely 1.68, 9.91, 18.13, 26.35, and 34.57 \((10^{-2})\) J corresponding to a drop height of 0.052, 0.302, 0.560, 0.814, and 1.068 (m) respectively.

4.3.2 Results and Discussion

*Analysis of Variance (Identification of important ITOF fabrication parameters)*

Data from the second, third and fourth impact levels were used for the ANOVA. This is because the first impact level seems to be very low and inadequate to cause the TL excitation of the ITOF. Earlier work by Womack et al [24] and by Olawale et al [27] reported a minimum impact
level of about $1.6 \times 10^{-2}$ J. The fifth impact level was not used because a large proportion of the samples were completely fractured by this impact level.

Figure 4.5 shows the normal plot of the standardized effect. It can be seen that three of the four factors investigated are significant. These factors are the ZnS:Mn/epoxy ratio, crystal size and the presence of cladding.

Figure 4.5: Normal plot of the standardized effects from impact level of 0.181 J.

The result from the ANOVA also collaborates this finding as shown in Table 4.3. The terms with the p value of less than 0.05 are significant considering a 95 per cent significant level. The result gives a $R^2$ value of 0.869 and a $R^2$ (adj) value of 0.753 that indicate that the statistical model accounts for 87% and 75% of the variability in the data.
Table 4.3: ANOVA result of estimated effects and coefficients for impact energy level of 0.181J.

<table>
<thead>
<tr>
<th>Term</th>
<th>Effect</th>
<th>Coeff.</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>-2.804</td>
<td>3.4295</td>
<td></td>
<td>-0.82</td>
<td>0.437</td>
</tr>
<tr>
<td>ZnS:Mn/epoxy ratio</td>
<td>17.592</td>
<td>8.796</td>
<td>3.4295</td>
<td>2.56</td>
<td>0.033</td>
</tr>
<tr>
<td>Crystal size</td>
<td>-3.811</td>
<td>-1.905</td>
<td>0.5638</td>
<td>-3.38</td>
<td>0.010</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>-9.079</td>
<td>-4.539</td>
<td>2.2553</td>
<td>-2.01</td>
<td>0.079</td>
</tr>
<tr>
<td>Cladding</td>
<td>-5.651</td>
<td>-2.825</td>
<td>0.5638</td>
<td>-5.01</td>
<td>0.001</td>
</tr>
<tr>
<td>ZnS:Mn/epoxy ratio * Crystal size</td>
<td>0.219</td>
<td>0.110</td>
<td>0.5638</td>
<td>0.19</td>
<td>0.851</td>
</tr>
<tr>
<td>ZnS:Mn/epoxy ratio * Coating thickness</td>
<td>9.860</td>
<td>4.930</td>
<td>2.2553</td>
<td>2.19</td>
<td>0.060</td>
</tr>
<tr>
<td>ZnS:Mn/epoxy ratio * Cladding</td>
<td>-1.264</td>
<td>-0.632</td>
<td>0.5638</td>
<td>-1.12</td>
<td>0.295</td>
</tr>
</tbody>
</table>

The main effect plots for the three impact levels are as shown in Figures 4.6, 4.7 and 4.8. The results clearly show that higher TL responses would be obtained from ITOF sensors with smaller crystal size and cladded optical fiber. The TL response also tends to increase with the ZnS:Mn/epoxy ratio (Figures 4.7 and 4.8). The observed low response at the higher ZnS:Mn concentration in Figure 4.6 is most likely because at this relatively low impact level, there was not sufficient energy to excite all the available crystals in the sensors.

Figure 4.6: Main effects plot at impact level of $9.91 \times 10^{-2}$ J.
The low TL responses associated with the uncladded sensors are caused by signal losses along the length of the optical fiber because of the removed cladding. For TL signals to be successfully transmitted along the length of the optical fiber, the refractive index of the core must be greater than that of the cladding:

\[ n_{\text{core}} > n_{\text{cladding}} \]  \hspace{1cm} (4.1)
The result shows that the ZnS:Mn/epoxy coating is not acting as an effective cladding for the uncladded ITOF sensor. Even if its refractive index is lower than that of the core, the interface between the coating and the core is large resulting in loss of the TL signals. A very important implication of this finding is that there is no need to use the more expensive larger-sized crystals. This will further help to make the ITOF sensor more economical. The results are in line with literature [128] where nano-sized ZnS:Mn gave better TL responses than micro-sized particles.

**SEM Characterization**

Figure 4.9 shows the SEM micrograph of a cut cross-section of an uncladded ITOF sensor. There is a distinct interface between the POF and the ZnS:Mn/epoxy coating (Figure 4.9a). The size of the interface is as high as 50µm (Figure 4.9b). This may explain the low TL responses associated with the uncladded ITOF sensor. There were significant TL signal losses along the length of the optical fiber into the interface because of the removed cladding. The ITOF coating cannot function as the cladding of the POF. The effective side coupling of the TL signals from the coating through the cladded ITOF shows the viability of the ITOF as a truly distributed sensor system for monitoring hidden damage in composite structures when the POF is completely coated with ZnS:Mn thin film. Furthermore, it would be easy to produce the ITOF sensor on an industrial scale.

![Figure 4.9](image_url)

**Figure 4.9:** (a) Cut cross-section of an uncladded ITOF sensor, (b) Interface between POF and ITOF sensor coating.

Samples of the ITOF sensor coating were studied with the FESEM to gain insight into the level of dispersion of the crystals in the epoxy system. Figure 4.10a shows that the crystals appeared to
be well dispersed in the epoxy matrix. Furthermore, the crystal size varies and there tends to be agglomeration of the crystal particles (Figure 4.10b). This highlights the importance of good fabrication methodology in order to ensure good dispersion of the crystals to get more predictable responses from the ITOF sensor.

![Figure 4.10: (a) Dispersion of ZnS:Mn in epoxy matrix (1:1) of the ITOF coating (b) the ZnS:Mn crystals.](image)

### 4.4 Design Parameters Evaluation with Sensors Fabricated by Mold Process

Figure 4.11 provides an overview of an enhanced fabrication process for the ITOF sensor. The sensors fabricated were made from 1 mm diameter polymer optical fiber (POF) manufactured by Mitsubishi Rayon Company (SH-2001-J). The POFs were cut into lengths of 900mm. Close to the center, the jacket of the POF was removed over a section of length 55mm (Figure 4.11b). This was coated with a mixture of polymer and the triboluminescent material (ZnS:Mn) to form the sensory receptor of the ITOF sensor (Figure 4.11c). The mixture was prepared by measuring and mixing the appropriate amount of the polymer (US Composites 635 thin film epoxy resin) and the hardener (ratio 3:1) for about 30 seconds. The appropriate amount of ZnS:Mn (supplied by Phosphor Technology, UK) was added and the mixture mixed by stirring manually for about 90 seconds. The mixture was degassed in a vacuum oven at a temperature of about 50°C for 10
It was then transferred into a prepared silicone molds by means of a pipette (Figure 4.12). Mold preparation involved primarily cleaning the mold with air under pressure and coating with release agent (Pol-ease 2500 by Polytek Development Corp.). The ITOF sensors were allowed to cure for about 12 hours before demolding. The use of the mold helps in the fabrication of ITOF sensors with a more uniform coating thickness.
4.4.1 Test Procedure
The $2^K$ factorial experimental design technique was used in determining the levels of three key design parameters that give enhanced TL responses in the ITOF sensor. The key design parameters investigated are the sensor thickness, ZnS:Mn/epoxy concentration, and the impact energy level. Table 4.4 highlights the levels of the parameters investigated. The samples were impacted with a small cylindrical steel mass in a custom-built impact rig (Figure 4.4) as described earlier.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Low level</th>
<th>High Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensor coating thickness (mm)</td>
<td>1.63</td>
<td>2.63</td>
</tr>
<tr>
<td>ZnS:Mn/epoxy concentration</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>Impact energy (J)</td>
<td>0.249</td>
<td>0.483</td>
</tr>
</tbody>
</table>

4.4.2 Results and Discussion

*Determination of key design factors’ levels*
Figures 4.13-4.15 show the surface and contour plots of the TL responses of the ITOF sensors. Figures 4.13(a) and 4.13(b) indicate that higher TL responses were obtained with the low coating thickness (1.63mm) and the high ZnS:Mn/epoxy weight fraction (0.5). The contour plot (Figure 4.13(b)) shows that with low coating thickness, it may be possible to reduce the ZnS:Mn/epoxy weight fraction without significantly lowering its TL performance over a given range. Similarly, Figure 4.14(a) and 4.14(b) indicate that higher TL responses were obtained with high ZnS:Mn/epoxy weight fraction and high impact energy levels.
Figure 4.13: Effect of sensor coating thickness and ZnS:Mn/epoxy weight fraction on ITOF sensors’ TL responses (a) surface plot (b) contour plot.
The low coating thickness (1.63 mm) and high impact level resulted in higher TL responses as highlighted by Figures 4.15(a) and 4.15(b). The contour plot (Figure 4.15(b)) shows that the ITOF sensor is very sensitive to impact energy at the low thickness level. It seems that at this low thickness level, all the impact energy levels investigated were sufficient to excite the available crystals to give the peak TL responses for that impact energy level range. There is also better side-coupling of the TL signals generated at impact because the crystals are positioned closer to the transmission component in the low thickness sensors.
The interaction plot (Figure 4.16a) shows some interaction between the ZnS:Mn/epoxy weight ratio and the coating thickness as indicated by the different slopes of the plotted lines. The 1.63mm sensors exhibited higher TL sensitivity when made of ZnS:Mn/epoxy (0.5 wt fraction) than when made of ZnS:Mn/epoxy (0.25 wt fraction). Significant interactions exists between the impact energy level and the coating thickness (Figure 4.16b), and the ZnS:Mn/Epoxy weight ratio (Figure 4.16c) as indicated by the non-parallel interaction lines. The 2.63mm sensors exhibited higher sensitivity at the high impact level investigated, compared to the 1.63mm
sensors. The higher impact energy tended to excite more crystals that are available in the large coating thickness, as well as better excite crystals located nearer to the transmission component.

![Image of Figure 4.16](image)

Figure 4.16: Interaction plot for the TL response of the ITOF sensor under impact load.

(polymer optical fiber). The peak TL responses of virtually all the available crystals in the small coating thickness seemed to have been reached at the lower impact energy level investigated (Figure 4.16b) as indicated by the peak mean TL response obtained. Consequently, ITOF sensors can be designed to have enhanced sensitivity to different damaging event severity based on the coating thickness. Low coating thickness with high sensitivity for low damage energy situations and high coating thickness for enhanced sensitivity at high damage energy situations. The coating thickness directly determines the number of crystals (for a given TL crystal weight fraction) available for excitation.

Figure 4.16c shows that at both the low (0.249J) and high (0.483J) impact levels, the ZnS:Mn/epoxy (0.5 wt fraction) sensors gave higher mean TL response compared to the ZnS:Mn/epoxy (0.25 wt fraction) sensors. The ZnS:Mn/epoxy (0.25 wt fraction) sensors exhibited very low sensitivity to the low impact energy (0.249J) investigated while exhibiting a high sensitivity at the high impact level (0.483J) studied. At the high impact energy level, the dampening effect of the high polymer content of the ZnS:Mn/epoxy (0.25 wt fraction) ITOF sensor was overcome and more energy made available to excite the ZnS:Mn crystals. There seemed to be less dampening effect in the ZnS:Mn/epoxy (0.5 wt fraction) sensors because of the reduced polymer content.
**Dynamic Mechanical Analysis (DMA) Characterization**

Dynamic Mechanical Analysis (DMA) was used to characterize the effect of ZnS:Mn content on the storage modulus and the glass transition ($T_g$) of the ITOF coating. Figure 4.17 shows a typical curve obtained from the DMA tests. The storage modulus was obtained from the storage modulus curve at a temperature of 25°C. The onset point of the storage modulus curve gives the glass transition temperature where the composite system starts to lose its mechanical strength.

![DMA plot from ITOF coating characterization.](image)

The $T_g$ increased with the inclusion of the ZnS:Mn crystals (Figure 4.18). It increased from a mean value of 44.23°C (pristine epoxy system) to 51.58°C (0.25 wt fraction), and to 50.74 °C (0.5 wt fraction) ZnS:Mn/epoxy. The high melting point (about 1500 °C) of the ZnS:Mn crystals contributed to the observed increment in the $T_g$ of the composite. Similarly, the mean storage modulus (Figure 4.19) increased from about 1.349 GPa (pristine epoxy) to 1.935 GPa (0.25 wt fraction ZnS:Mn/epoxy) and to 2.254 GPa (0.5 wt fraction ZnS:Mn/epoxy). The inclusion of 25% and 50% (by weight) of ZnS:Mn crystals in the epoxy system resulted in 43.44% and 67.09% enhancement respectively of the storage modulus of the ITOF coating. The ZnS:Mn crystals seem to have acted as particulate reinforcements in the epoxy system because of its higher elastic Young modulus of $6.72 \times 10^{11} \text{ dyn/cm}^2$ (67.2 GPa) [128]. Consequently, the ZnS:Mn/epoxy system of the ITOF sensor exhibits enhanced thermo-mechanical properties which is desirable in a sensor system.
Characterization of ITOF Sensor Response under Impact Loads

This characterization was done by striking the ITOF sensors at four impact energy levels namely 0.1244, 0.2730, 0.4216 and 0.5702 J. This corresponds to a constant impact energy increment of 0.1486 J. Six ITOF sensors were tested at each impact level and the TL responses monitored with the PMT. The ITOF sensors had a ZnS:Mn/epoxy weight fraction of 0.5 and two coating thicknesses (1.63 and 2.63 mm) were investigated. The sensors gave increasing average TL responses with increasing impact energy (Figure 4.20). The low coating (1.63 mm) sensors however gave higher mean TL responses compared to the large coating (2.63 mm) sensors. A linear relationship was observed between the TL response and the applied impact energy. This linear relationship was maintained at all impact energy investigated for the large coating (2.63 mm) sensors. Similar relationship was observed with the small coating (1.63 mm) sensors up to the third impact energy level (0.4216J) investigated. A sharp jump in the TL response was however observed at an impact energy level of 0.5702J.

Figure 4.18: Effect of ZnS:Mn loading on the mean T_g of ITOF coating.

Figure 4.19: Effect of ZnS:Mn loading on the mean modulus of the ITOF coating.
In comparison, Womack et al [24] reported a minimum excitation energy of about 0.016J for direct impact excitation of ZnS:Mn crystals. Higher minimum impact energy is however required for TL excitation of ITOF sensors, depending on the coating thickness. The impact energy applied to the coating is shared between the epoxy matrix and the dispersed ZnS:Mn crystals. Since the applied energy is shared, more energy is required to be applied on the ZnS:Mn-epoxy system before the crystals can experience sufficient energy to cause their excitation. This explains why the observed minimum energy for excitation of the ITOF was higher than that reported by Womack et al.

Furthermore, Womack et al observed a linear but rapid increase (large slope) in the TL response up to an impact energy level of about 0.26 J and then smaller but also linear increases in the TL responses (gentle slope) with increase in the impact energy levels. Gentle and linear slopes were observed for the ITOF sensors. The observed jump in the TL mean response of the 1.63 mm coating ITOF is similar to what was observed by Womack et al [24] with the large slope up to the impact level of 0.26 J (Figure 2.21). According to Womack et al, in this region (less than 0.26 J), the crystals were being fractured because they were struck directly. As the impact energy was increased, more crystals were fractured and more increases in the TL signals were observed. For the ITOF, because the crystals were embedded within the epoxy matrix, the crystals were not fractured. More energy was required to fracture them. Hence, the increase in TL responses were
linear and incremental with increase in the impact energy because of the dampening effect of the epoxy matrix (Figure 4.21a). Thus, elastico-TL and plastico-TL dominated the TL mechanism experienced by the sensors. At the impact energy of 0.5702 J however, the applied energy was sufficiently high to cause the fracture of the ITOF coating and the embedded TL crystals leading to fracto-TL as evident by the jump in the TL signal similar to that obtained by Womack et al during direct impact of the TL crystals. Experience gained with working with the ITOF has shown this characteristic jump in the TL intensity signal when fracture or microcracks occur.

The TL crystals in the thinner (1.63 mm) ITOF coating experienced a higher impact energy than the crystals in the larger coating ITOF. This may be attributed to the much higher density of ZnS:Mn (4.2 g/cm³) which is about 3 times that of the epoxy matrix (1.2-1.5 g/cm³). This means in terms of volume, there are about 3 times more epoxy than ZnS:Mn crystals for equal weight fraction. Since the crystals are located within the epoxy matrix of the coating, the energy has to be transmitted through the epoxy to the crystals. While ZnS:Mn has a Young modulus of about 67.2 GPa, epoxy has a Young’s modulus of about 2.4 GPa. Hence, the epoxy matrix may create a dampening effect that further reduces the impact energy experienced by the crystals within it. As will be shown later, the ITOF with its coating has a flexural modulus value of about 3.4GPa.

The TL crystals located nearer to the outer diameter of the coating are more likely to experience higher impact energy. The TL emissions may however not be successfully coupled into the POF with the increased crystal distance from the POF because of TL emission absorption by the surrounding opaque matrix and crystals. The larger the coating thickness therefore, the more pronounced are these effects (Figure 21b). This explains why the smaller coating thickness consistently resulted in higher TL response for any given impact energy level.
Figure 4.21: Interval plot with one standard error from mean of TL response of ITOF sensor (a) 1.63mm coating thickness (b) 2.63 coating thickness.

4.5 Summary

The ITOF sensor has the potential to revolutionize the structural health monitoring of composite structures, particularly cementitious composites like concrete structures. This study has identified the levels of key sensor design parameters that give enhanced TL performances of the ITOF. The ITOF sensor with the smaller coating thickness (1.63mm), higher ZnS:Mn concentration (0.5), and smaller crystal size exhibits enhanced TL responses on impact. The DMA characterization reveals that there is an increase in the $T_g$ and storage modulus with the inclusion of the ZnS:Mn crystals into the epoxy system. These imply that the inclusion of ZnS:Mn into the epoxy does not degrade the thermo-mechanical properties of the system. Furthermore, it has been shown that the
ITOF sensor can discriminate among different energy levels and is able to detect multiple
damage events provided the sensor has not been fractured. An improved fabrication process was
also developed. It was also shown that although the ZnS:Mn retained its TL properties in the
epoxy matrix of the ITOF, its TL excitation behavior is however different. This is because the
epoxy matrix introduces a dampening effect coupled with the opacity effect. The sensor can be
designed to accommodate the expected damaging energy levels based on the sensor size.
CHAPTER FIVE

ITOFSENSOR IMPACT EXCITATION MODEL

A lot of research work has gone into the characterization of the TL performance of TL crystals under direct impact loading. The ITOF sensor provides a different kind of system in which the TL crystals are randomly dispersed in an epoxy matrix. The excitation of the TL crystals in this composite system is expected to be different because of the interactions between the crystals and matrix during loading. Hence, this needs to be studied. Furthermore, there are two key design parameters that can be readily used to tailor the behavior of the sensor for enhanced TL-based sensing performance. These are the sensor size and the volume fraction of the TL crystals in the coating. The modeling effort will draw on existing knowledge to establish a relationship between the TL intensity response of the ITOF as a function of sensor size and volume fraction of the sensor coating for a given impact energy level.

5.1 Theoretical Model

Triboluminescence may be divided into three types: namely (1) elastico-, (2) plastico- and (3) fracto-triboluminescence [22]. Elastico-TL is luminescence produced during the elastic deformation of solids, where neither fracture nor plastic deformation is required. Elastico-TL in ZnS:Mn starts at a pressure of about 1MPa ($10^6$ Nm$^{-2}$) while plastico-TL and fracto-TL start at about 30MPa and 100MPa respectively [21, 22, 128]. This implies that a minimum stress level of about 1MPa is required by ZnS:Mn crystals before any TL signal can be generated and detected. Based on these, the following assumptions have been made for the model development:

1. Perfect bonding between the TL crystals and the epoxy matrix.
2. Stress level generated in the TL crystals is within the elastic limit of the crystals

The maximum TL intensity produced by applying a load onto ZnS:Mn nanoparticles may be given as [128]:

$$I_m = \frac{\eta \sigma_0^2 \delta^2}{2} \quad (1a)$$

$$\sigma_0 = \left(\frac{2I_m}{\eta \alpha_0}\right)^{1/2} \quad (1b)$$
where $d_o$ is the localized piezoelectric constant near the Mn$^{2+}$ centers in ZnS:Mn nanoparticles, $\sigma_o$ is the final stress, $\eta$ is the efficiency of the radiative emission from Mn$^{2+}$ centers during the electron-hole recombination, and $\alpha$ is a constant that is related to the density of the Mn$^{2+}$ centers and the density of electrons in shallow traps. Equation (1) implies that the peak TL intensity will increase quadratically with $\sigma_o$, the final pressure or stress experienced by the TL crystal. At constant deformation rate however, the peak intensity will increase linearly with the applied pressure:

$$I_m = \frac{\eta ad_o^2 \sigma_o}{2}$$  \hspace{1cm} (2)

$$\sigma_o = \frac{2I_m}{\eta ad_o^2}$$  \hspace{1cm} (2b)

**Model 1**

Considering a unit length of ITOF sensor under impact loading (Figure 5.1), the fraction $f$ of the impact energy absorbed by the ITOF sensor may be given as:

$$fE_l = E_{coating} + E_{pof}$$  \hspace{1cm} (3)

or

$$fE_l = E_{Te} + E_p + E_{pof}$$  \hspace{1cm} (4)

![Figure 5.1: Schematic of ITOF sensor under impact loading.](image-url)
where $E_i$ is the energy from the impactor, $E_{coating}$ is the energy absorbed by the coating, $E_{pofo}$ is the energy absorbed by the polymer optical fiber, $E_{Tc}$ is the energy absorbed by the TL crystals of the ITOF coating, and $E_p$ is the energy absorbed by the polymer component of the ITOF coating. The energy absorbed by the various components of the ITOF coating can be given in terms of the specific absorption energy $\xi$ defined as the energy absorbed per unit mass of a material [158] as:

$$fE_i = \xi_{Tc}m_{Tc} + \xi_p m_p + E_{pofo} \quad (5a)$$

or

$$fE_i = \xi_{Tc} \rho_{Tc} v_{Tc} V + \xi_p \rho_p v_p V + E_{pofo} \quad (5b)$$

where $m_{Tc}$ and $m_p$ denote the mass of the TL crystals and polymer components of the ITOF coating respectively; $V$ denotes the total volume of the coating in the region of impact; $v_{Tc}$ and $v_p$ denote the volume fraction of the TL crystals and polymer components of the coating respectively.

The specific absorption energy is given as a function of the mean crushing stress $\sigma$ and density $\rho$ of the material as [158]:

$$\xi = \sigma / \rho \quad (6)$$

Equation (5b) may be rewritten as:

$$fE_i = \sigma_{Tc} v_{Tc} V + \sigma_p v_p V + E_{pofo} \quad (7)$$

The stress available to cause the excitation of the TL crystals can be given as:

$$\sigma_{Tc} = \frac{fE_i}{v_{Tc} V} - \frac{\sigma_p v_p}{v_{Tc}} - \frac{E_{pofo}}{v_{Tc} V} \quad (8)$$

The volume of the impacted coating area (considering a length $d$ corresponding to the diameter of the impactor) is given as:

$$V_i = \pi (R^2 - r^2) d \quad (9)$$
where $R$ is the radius of the ITOF coating and $r$ is the radius of the POF. Substituting in Equation (8) gives:

$$\sigma_{TC} = \frac{f_{EI}}{v_{TC} \pi (R^2 - r^2) d} - \frac{\sigma_{pVp}}{v_{TC}} - \frac{E_{pof}}{v_{TC} \pi (R^2 - r^2) d}$$  \hspace{1cm} (10)

Substituting Eqn (1b) into Eqn (10) gives

$$I_m = \left[ \frac{f_{EI}}{v_{TC} \pi (R^2 - r^2) d} - \frac{\sigma_{pVp}}{v_{TC}} - \frac{E_{pof}}{v_{TC} \pi (R^2 - r^2) d} \right]^2 \frac{\eta a d_a^2}{2}$$  \hspace{1cm} (11)

but

$$v_{TC} = \frac{m_{TC}}{\rho_{TC}}$$  \hspace{1cm} (12a)

$$v_{TC} = \frac{m_{TC}'}{\rho_{TC}} M$$  \hspace{1cm} (12b)

$$V = \left( \frac{m_{TC}'}{\rho_{TC}} + \frac{m_p'}{\rho_p} \right) M$$  \hspace{1cm} (13a)

where $m_{TC}'$ and $m_p'$ is the mass fraction of the TL crystals and the epoxy respectively in the ZnS:Mn/epoxy composite and $M$ is the total mass of the composite.

$$V = \left( \frac{m_{TC} \rho_p + m_p \rho_{TC}}{\rho_{TC} \rho_p} \right) M$$  \hspace{1cm} (13b)

Substituting Eqn 13b into Eqn 12b gives

$$v_{TC} = \frac{m_{TC}'}{\rho_{TC}} M \times \frac{\rho_{TC} \rho_p}{M (m_{TC} \rho_p + m_p \rho_{TC})}$$  \hspace{1cm} (14a)

$$v_{TC} = \frac{m_{TC}' \rho_p}{m_{TC} \rho_p + m_p \rho_{TC}}$$  \hspace{1cm} (14b)

Similarly,

$$v_p = \frac{m_p \rho_{TC}}{m_{TC} \rho_p + m_p \rho_{TC}}$$  \hspace{1cm} (15)
Substituting Eqn (14b) and Eqn (16) in to Eqn (11) gives

\[
I_m = \left[ \frac{f E_i}{\pi (R^2 - r^2) d} \times \frac{m_T^i \rho p + m_T^p \rho_T c}{m_T^c \rho p} - \frac{\sigma_p m_p^i \rho_T c}{m_T^c \rho p} - \frac{E_{p0f}}{\pi (R^2 - r^2) d} \right] \frac{m_T^c \rho p + m_T^p \rho_T c}{2} \eta d_0^2
\]

Model 2

If a fraction \( f \) of the elastic energy of a cylindrical impactor of diameter \( d_i \) is given to the ITOF coating of the sensor consisting of the epoxy and ZnS:Mn crystals and POF with a total volume \( V \) under the impactor, the elastic energy can be given as [128]:

\[
f E_i = \frac{\sigma_0^2 V}{2Y}
\]

where \( Y \), \( E_i \), and \( \sigma_0 \) are the Young’s modulus of the sensor, impact energy and maximum value of the impact stress respectively. Equation (18) may be written as:

\[
\sigma_0^2 = \frac{2 f E_i Y}{\pi R^2 d_i}
\]

where \( R \) is the radius of the ITOF sensor.
Substituting Equation 19 into Equation 1 gives

\[ I_m = \frac{2f\eta d_0^2 E_i Y}{\pi R^2 d_i} \]  

(20)

Equation (20) is based on the assumption that the coating consists purely of TL crystals. To take account of the available TL crystals in the coating, the volume fraction term is included:

\[ I_m = \frac{2f\eta d_0^2 E_i Y}{\pi R^2 d_i} v_{TC} \]  

(21)

Substituting Eqn 14 into Eqn 21 gives

\[ I_m = \frac{2f\eta d_0^2 E_i Y}{\pi (R^2)d_i} \times \frac{m_{TC} \rho_p}{m_{TC} \rho_p + m_p \rho_{TC}} \]  

(22)

or

\[ I_m = \frac{8f\eta d_0^2 Y}{\pi d_i} \times \frac{E_i}{(D^2)} \times \frac{m_{TC} \rho_p}{m_{TC} \rho_p + m_p \rho_{TC}} \]  

(23)

where \( D \) is the diameter of the ITOF sensor. The factor \( v_{TC} \) is the volume fraction of triboluminescent crystals in the coating. When the coating is purely TL crystals, all the generated stress is available to excite the crystals \( v_{TC} = 1 \). When there are no crystals in the coating, \( v_{TC} = 0 \), and no TL signal will be generated.

Eqn (21) implies that the higher the energy of impact, the higher the stress level generated in the ITOF coating to cause higher intensity TL responses in accordance with Eqn (1). A linear relationship exists between the peak TL intensity and the impact energy. A linear increase in the sensor coating radius (thickness) will result in a quadratic order of reduction in the expected TL response.

### 5.2 Model Validation

Figure 5.2 is an overview of the model variables that were investigated and the measured response. An attempt was made to validate the model by subjecting the fabricated ITOF sensor samples to impact loading with a custom-built impact rig described earlier (Figure 4.4). Both
ends of the ITOF sensors were connected to a photodetector (photomultiplier tube) to ensure that all the TL signals generated at impact were detected.

![Diagram](image)

**Figure 5.2:** Overview of the model’s variables, input and output.

### 5.3 Results and Discussion

Table 5.1 is a data set for four different types of ITOF sensor configuration tested under the same impact energy level of 0.199 J. The standard error plots were constructed for each sensor configuration as in Figure 5.3. The standard error plot gives an indication of the spread of the experimental data around the mean.
Table 5.1 TL responses from different ITOF sensor configuration based on experimental result (TLexp) and model result (TLmodel) under impact energy of 0.199 J.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>x1</th>
<th>x2</th>
<th>Y1</th>
<th>Y2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sensor diameter (mm)</td>
<td>ZnS:Mn weight fraction</td>
<td>TLexp (AU)</td>
<td>TLmodel (AU)</td>
</tr>
<tr>
<td>1</td>
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<td>0.293</td>
<td>0.044</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
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<td>0.176</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
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<td>0.052</td>
<td>0.176</td>
</tr>
<tr>
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<tr>
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<td>0.5</td>
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<tr>
<td>12</td>
<td>6</td>
<td>0.5</td>
<td>0.029</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Figure 5.3 shows a reduction in the mean TL signal with increase in the sensor diameter for the two different TL crystal weight fractions investigated. The variation in the observed TL responses is greatest in the 3mm diameter and 0.5 ZnS:Mn weight fraction sensor. Generally, the small coating ITOF sensors exhibited higher variability in their TL responses.
To gain insights into the cause of the variations in the TL responses of the tested sensors, they were studied with the FESEM.

**Uniformity of Coating**

As noted in Table 5.1, Sensor 2 gave a significantly higher TL signal value (0.617 AU) than Sensor 3 (with a TL signal value of 0.052 AU) though they had the same configuration (TL crystal content of 0.25 wt fraction and sensor diameter of 3mm) and were impacted with the same impact energy level. Figure 5.4 shows FESEM micrographs of the cross-sections of sensors 2 and 3.

Figure 5.3: Interval plot (one standard error from the mean) of TL responses of tested ITOF sensor under impact load of 0.199 J.
Figure 5.4: FESEM micrographs of cross-section of a) Sensor 2 and b) Sensor 3.

Figure 5.4a shows that Sensor 2 has the TL coating more uniformly positioned around the transmission component (polymer optical fiber) than Sensor 3 (Figure 5.4b). The more uniform coating in Sensor 2 ensures that at any point around the sensor’s circumference, there are equal and greater chances of the crystals being excited and the signals being successfully coupled into the POF for onward transmission thereby resulting in higher TL signal value. In the case of Sensor 3 however, if the impactor strikes the top left section of the sensor (Figure 5.4b), the crystals will experience higher impact energy because the coating is very thin at this section. In addition, the signals will be more readily coupled into the POF because of the smaller travel distance. Because of these two reasons, we would expect higher TL signal from Sensor 3 if the impactor strike at this section.

The fact that less than 30% of Sensor’s 3 cross-section has this low thickness (~300 μm) greatly reduces the probability of this happening. The low signal from Sensor 3 suggests that the impactor may have struck the sensor at the thicker coating section. In the thicker coating section, less energy is available to excite the crystals. In addition, the portion of the TL crystals at the outer edge will experience higher impact energy but because of the longer travel distance to the POF, there would be less efficient TL emission coupling, leading to a low TL signal value.

Similarly, non-uniform coating of the sensors may be observed in Figure 5.5. Sensor 8 may have been impacted at the thicker section of the sensor resulting in the relatively lower TL signal of
0.314 (AU) while Sensor 9 may have been struck at the thinner section resulting in the higher TL signal of 1.618 (AU).

Figure 5.5: FESEM micrographs of sensors’ cross-section showing non-uniform coating a) Sensor 8 and b) Sensor 9.

**Crystal Distribution within a Sensor**

To study the dispersion of the TL crystals within a sensor, the cross-section of the sensors were examined under the FESEM. The sensor cross-section was divided into 4 parts (quadrants) namely the top, bottom, left and right sections of the sensor’s cross-section. The coating of the sensors were viewed along the four perpendicular lines (axes) close to the interface between the coating and the POF. The examination revealed an uneven dispersion of TL crystals in the coating around the POF of the sensor. Figures 5.6a (top section) and 5.6c (left section) show lower TL crystal contents compared to Figures 5.6b (bottom section) and 5.6d (right section). While a number of single crystals could be observed in Figures 5.6a and 5.6c, there are agglomerations of TL crystals forming clusters in Figures 5.6b and 5.6d. The observed differences in dispersion is believed to be caused by the settling of the ZnS:Mn crystals in the epoxy because of the crystals’ high density (4.2 g/cm\(^3\)) relative to the density of the epoxy matrix of the coating. This has been reported in earlier work by Dickens et al [159]. This suggests that the TL emissions and TL signals detected when the impactor strikes the sections shown by Figures 5.6b and 5.6d will be higher than when it strikes the sections represented by Figures 3a and 3c because of the higher TL crystal concentration.
Similar non-uniformity in the dispersion of the crystals within the coating was observed in other sensor sections studied. Figure 5.7 shows the FESEM micrographs for Sensor 3. In Figure 5.7a (top section), there tends to be a uniform dispersion of the ZnS:Mn crystals within the matrix. In Figure 5.7b (bottom section) however, the crystals tend to agglomerate and form clusters rather than being uniformly distributed within the matrix. Figure 5.7c (left section) and Figure 5.7d (right section) have lower TL crystals content and poorer dispersion compared to Figure 5.7a (top section) and Figure 5.7b (bottom section).
Figure 5.7: FESEM micrographs for Sensor 3 showing unequal dispersion of ZnS:Mn crystals within the ITOF sensor coating a) top, b) bottom, c) left and d) right sections.

From the above, it can be concluded that dispersion of the crystals in the epoxy matrix of the ITOF sensor coating is certainly an issue that needs to be overcome in order to have a sensor with consistent responses. The use of TL crystals with density values close to that of the matrix will help to reduce the settling effect problem. The fabrication process has to be improved to enable more uniform coating and TL crystal dispersion. This is subject to future work. Consequently, the model could not be validated.

5.4 Summary

An attempt was made to develop two models based on the elastic energy transferred onto an ITOF sensor under impact loading. The models aim at predicting the triboluminescent signal at a given impact energy as a function of key sensor design parameters namely the sensor diameter.
and the volume fraction of the TL crystals in the ZnS:Mn/epoxy composite of the sensor coating. Attempt was made to validate one of the models experimentally. Experimental results showed high variability in the TL behavior of the sensors tested. Microscopic studies show that non-uniform coating and poor TL crystals dispersion in the coating are responsible for the observed high variability in the tested sensors’ TL behavior. Consequently, the model could not be validated. While the model was based on the assumption of elastico-TL, experimental results have shown strong indication of multiple TL excitation mechanisms at work. As the existing knowledge gap in the cause of the TL mechanism is closed, effective models can be developed.
CHAPTER SIX
CHARACTERIZATION OF THE DAMAGE MONITORING BEHAVIOR OF THE ITOF SENSOR

Before the ITOF sensor can be effectively used in composite systems as an in-situ damage monitoring sensor system, its triboluminescent behavior under critical loading conditions has to be understood. To do this, the TL behavior of the ITOF sensor under flexural loading was investigated by subjecting it to 3 point bend tests (PBTs). The tests provided insights into the behavior of the sensor when integrated into structural components subjected to flexural loads such as the girders of a bridge. The fracture surfaces of the sensors after the flexural tests were studied to gain insight into the TL excitation mechanism. Raman spectroscopy was used to characterize the properties of the TL crystals (ZnS:Mn) before and after being incorporated into the ITOF coating. Dynamic mechanical analysis was used to characterize the stress-strain behavior of the sensor with high precision.

6.1 Materials and Methods

This section describes the materials, fabrication and experimental setup employed in characterizing the damage monitoring behavior of the ITOF sensor.

6.1.1 Sensor Fabrication

ITOF sensors with rectangular cross-section with dimensions of 3 x 3 x 50mm were fabricated for the flexural test and characterization. The width and thickness were chosen to be close to the radius of the cylindrical ITOFs. A waterjet cutting machine (Omax, Inc) was used to cut aluminum plate of 3.28mm thickness into bars of dimensions 3.28 x 3.28 x 50mm. Eight of these bars were glued to the base of a prepared topless rectangular box made of plexiglass (Figure 6.1) with an epoxy adhesive. After the curing of the adhesive, release agent was applied on the aluminum bars and the internal surfaces of the plexiglass box. After drying, appropriate quantities of silicone and hardener (Poly 75-75) were measured and manually mixed with a wooden stirrer for about 10 minutes according to the directions from the manufacturer (Polytek Development Corp.). The mixture was poured into the prepared mold and allowed to cure for 24 hours before demolding. Slits were cut in the mold to allow for easy fiber placement.
The POFs were prepared by manually removing the protective jacket with a fiber cutter tool to expose about 60mm surface length of POFs. The exposed portion of the fibers were then placed in the silicon mold to on which release agent had been applied much earlier to ensure proper drying. The appropriate quantity of ZnS:Mn from Phosphor Technology, UK and epoxy (US Composites, Inc) are measured and mixed manually. Figure 6.2 is a flow chart for the fabrication of the ITOF sensor while Figure 6.3a shows one of the fabricated molds and Figure6. 3b) shows the sensors fabricated.

Figure 6.2: ITOF sensor fabrication process.
6.1.2 Flexural Test

A Shimadzu micro-tensile testing machine (Figure 6.4) with 5KN capacity was used to apply flexural load on the sensors. Two loading rates (1mm/min and 10mm/min) were investigated. The TL signals generated during loading was detected with a photomultiplier tube (PMT) supplied by Hamamatsu, Japan. Both ends of POF from the sensor were connected to the PMT to ensure that no signal was lost. The ends were carefully polished with a grade 1200 sandpaper before connecting to the PMT. The PMT was powered with an Agilent E360A triple output DC power supply at 0.5V. A custom-written program based on Matlab was used to control the operation of the PMT and to display the TL response values and profiles through a National instrument NI-USB-6210 data acquisition device.
6.1.3 Characterization Techniques

Raman spectroscopy was performed using Renishaw in Via Raman Microscope (Figure 6.5) to study the chemical and structural properties of the ZnS:Mn crystals before and after incorporating into the epoxy component of the ITOF coating and after undergoing the fabrication process. Dynamic mechanical analysis (DMA) was used to characterize the stress-strain behavior of the sensor (Figure 6.6). Three-point bend tests were (3PBT) was performed using the TA Instrument, Inc DMA 2980 under controlled force rate mode. A loading rate of 1N/min was applied. The span of the setup was 20mm. The data from the tests were analyzed using Universal
Figure 6.5: Renishaw in Via Raman Microscope for Raman spectroscopy analysis.

Figure 6.6: a) Stress-strain characterization with TA Inc DMA 2890, b) furnace exposed with sensor loaded onto the clamp.

Analysis 2000. Morphological study was conducted using Field Emission Scanning Electron Microscope (JEOL JSM-7401F) to have details about the ZnS:Mn crystals dispersion in the epoxy matrix and to understand the interface between the POF and the ITOF coating (Figure 6.7). All the samples were coated with gold particles before viewing under the FESEM.
Furthermore, the fractured surfaces of some of the failed samples were studied under the FESEM. The surfaces of the samples were inspected for micro-cracks and hidden cracks with OLYMPUS BX40 Microscope (Figure 6.8).

Figure 6.7: Field Emission Scanning Electron Microscope (JEOL JSM-7401F) for morphological characterization.

Figure 6.8: Surface crack characterization with OLYMPUS BX40 Microscope.
6.2 Results and Discussion

The results from the tests are presented and discussed in the following sections.

6.2.1 Raman Spectroscopy

Figure 6.9 shows the Raman spectra of ZnS:Mn/epoxy, epoxy polymer, and ZnS:Mn. The ZnS:Mn micro-crystals have their Raman spectra (curve 1) with typical peaks at 300, 350, 396 and 670 cm\(^{-1}\) [160]. The Raman bands at 300, 350, 396 and 670 cm\(^{-1}\) of the ZnS:Mn micro-crystals remained unchanged in the ZnS:Mn/epoxy composite system as indicated in Figure 6.9 (curve 3). It can be inferred that the ZnS:Mn in the ZnS:Mn/epoxy composite has its chemical and structural properties unchanged, thereby effectively preserving the TL property of the ZnS:Mn crystals.

The bands at 638, 672, 821, 1113, 1188, 1455 and 1600 cm\(^{-1}\) clearly correspond to the finger print of the pure epoxy phase (curve 2) [161] in which the ZnS:Mn micro-crystals were dispersed in fabricating the TL film coating of the ITOF. The chemical and structural information (Raman bands) have been compared to that of the control epoxy sample as reported in Figure 6.9 (curve 2). The band at 1590 cm\(^{-1}\) (curve 2) was slightly upwardly shifted by 20 cm\(^{-1}\) to 1610 cm\(^{-1}\) (curve 3). This is an indication of interactions between the polymeric chain and inorganic TL crystals that strengthen and stabilize the TL crystals with the epoxy component of the coating around the ITOF sensor. Based on these interactions, a strong bond and a good interface is expected to develop between the ZnS:Mn and the epoxy component of the ITOF coating. This is critical for effective load transfer through the matrix to the crystals for TL excitation during damaging events.

![Raman spectra](image)

Figure 6.9: Raman spectra of 1) ZnS:Mn(1:1), 2) epoxy, 3) ZnS:Mn:epoxy.
6.2.2 Stress-strain Characterization with DMA

Table 6.1 summarizes the data from the stress-strain characterization of the ITOF sensor (50:50 wt percent) with DMA. Two types of samples were fabricated, a set of four without the POF incorporated and another set of four samples with the POF present.

Table 6.1: Result of stress-strain characterization with DMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus (GPa)</th>
<th>Strain (%)</th>
<th>Stress at observed strain (MPa)</th>
<th>Size w X t (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-001</td>
<td>2.805</td>
<td>0.75</td>
<td>20.65</td>
<td></td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-002</td>
<td>2.992</td>
<td>0.76</td>
<td>22.59</td>
<td>3.48, 2.62</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-003</td>
<td>3.324</td>
<td>0.63</td>
<td>20.67</td>
<td>3.25, 2.92</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-005</td>
<td>3.580</td>
<td>0.71</td>
<td>20.65</td>
<td>3.25, 2.83</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-006 (with POF1)</td>
<td>4.383</td>
<td>0.65</td>
<td>20.71</td>
<td>3.25, 2.83</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-007 (with POF2)</td>
<td>2.701</td>
<td>0.79</td>
<td>20.71</td>
<td>3.25, 2.83</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-008 (with POF3)</td>
<td>3.995</td>
<td>0.57</td>
<td>20.70</td>
<td>3.25, 2.83</td>
</tr>
<tr>
<td>Rect ITOF 50-50 ZnSMn-Epoxy_No POF-010 (with POF4)</td>
<td>2.507</td>
<td>0.85</td>
<td>20.63</td>
<td>3.25, 2.83</td>
</tr>
</tbody>
</table>
The first two samples in Table 6.1 were loaded at a force rate of 1N/min (~0.04 strain percent/min) while all the other samples were loaded at 3N/min (~0.10 strain percent/min recommended loading rate for ASTM D3039/D4065) at room temperature (23°C). The span for all the samples was 20mm. This test indicates that the ITOF coating with the POF (50:50 wt fraction) behaves as a linearly elastic material up to a strain of over 0.6% (at loading rate of 3N/min or 0.104% strain/min) as illustrated in Figure 6.10. The ITOF sensor therefore has a strain level that is over 40 times that of concrete with a strain value of about 0.015%. Relatively large crack widths can therefore be monitored in concrete structures without damaging or fracturing the ITOF coating. This will help to prolong the life of the ITOF sensor on critical civil infrastructure and allow for repeated multiple usage. The mean flexural modulus for the sensor from the DMA 3PBT was 3.40GPa.

Figure 6.10: ITOF sensor (50:50 wt percent) exhibits linear elastic behavior above 0.6% strain.
6.2.3 Triboluminescent Behavior under Flexural Loading

Figure 6.11 shows the typical TL response from the ITOF sensor at the instant of failure of the beam under flexural loading. The loading profile clearly indicates that the sensor exhibits brittle failure mode (Figure 6.11a) as highlighted by the sudden drop in the load carrying capacity at the instant of failure. In addition, the capability of the sensor to provide real time damage monitoring is thus demonstrated by the sudden rise in TL signal value at the instant of failure. The high efficiency of the side coupling attained with the ITOF is highlighted by the high signal to noise ratio observable in Figure 6.11b. The clear signal at the instance of damage drastically reduces the complexity of signal processing and damage identification. Excessive data and complexity of signal processing for damage identification have been two of the main challenges militating against the wide use of structural health monitoring systems in engineering structures.

Figure 6.11: a) ITOF sensor under 3 PBT loading condition, b) real-time damage sensing with ITOF sensor.

The TL emission profile from the signal detected on the brittle failure of a sensor can provide an insight into the nature of the failure experienced by the sensor. The profile consists of two main parts (Figure 6.12). There is the rapid signal rising component with a very steep slope and the extended signal-decaying component. The time duration for the signals was 2-3ms, similar to that reported by Hollerman group. The TL profile duration indicates that the sensor experienced brittle failure. The prompt and sudden nature of the failure caused the excitation of all the crystals on the fracture path at the same instance causing all the signals to be detected as a single
profile similar to that observed by Hollerman et al [152] during direct impact striking of ZnS:Mn crystals.

Figure 6.12: Typical TL emission profile from the brittle failure of the ITOF sensor under flexural loading.

Figure 6.13 shows the result of tests aimed at investigating the response of the ITOF sensor to different loading speeds. The general trend is that the higher test speeds resulted in higher failure stresses and higher TL signals at damage. This may imply that the ITOF sensor can be sensitive to damage-causing events such as impact loads.

Figure 6.13: Effect of loading rate on ITOF sensor damage monitoring behavior.
In addition, a comparative study was carried out to evaluate the possibility of increasing the TL damage sensing performance of the ITOF sensor by increasing the weight percent of the ZnS:Mn in the sensor coating from 50 to 60%. Ten samples were tested under 3PBT loading condition at a loading rate of 1mm/min. Figure 6.14 shows that both sensor systems exhibited an increase in the TL signal peak value with increase in the failure stress. The 50:50 weight percent ITOF sensors exhibited higher TL signals (higher signal-to-noise ratio) than the 60:40 weight percent ITOF sensors. Although the 60:40 weight percent ITOF sensors have a higher quantity of ZnS:Mn crystals that should result in higher TL signals being generated at fracture, fabrication limitations adversely affected its TL sensing capability.

There tended to be insufficient quantity of epoxy in the ZnS:Mn/epoxy mixture because of the high ZnS:Mn content. The resulting highly viscous mixture made the effective coating of the POF by infusion in the molds very difficult. All these resulted in the fabrication of 60:40 ITOF sensors with many fabrication defects such as voids and poor interfaces as will be shown with surface cracks characterization (Section 6.2.4) and morphological characterization with the FESEM (Section 6.2.5). This is believed to be responsible for the lower TL outputs compared to the 50:50 ITOF sensors. This argument is supported by the fact that the fifth sample tested for the 60:40 sensors had a very high TL response well above 2.5V.

Figure 6.14: TL sensing performance of two ITOF sensor systems by weight percent.
6.2.4 Surface Cracks Characterization

The surfaces of the 60:40 weight percent ITOF sensors that did not fracture but recorded a loss in their load carrying capacity (failure) were examined under the optical microscope in order to verify the source and type of TL signals detected. Figure 6.15 shows the typical micrograph from a sensor that failed without any micro-crack on its surface. It is very likely that internal micro-cracks occurred within the system because there was definitely a lost in the load carrying capacity as detected by the MTS universal testing machine. Consequently, the ITOF sensor has the capability to undergo internal micro-cracking that results in TL responses with high signal-to-noise (SNR) when subjected to damaging load level. The high SNR resulted from the fracto-TL mechanism resulting from the micro-cracks.

Figure 6.15: Typical surface micrograph of ITOF samples showing no micro-cracks after 3 point bend test.

Microscopic examination of the surface of one of the sensors with surface defects revealed relatively large surface defects such as shown in Figure 6.16a. The sample had a relatively low failure stress of 23.74MPa and a relatively low TL signal level of 0.207V at failure. Figure 6.16b shows a micro-crack on the sample’s surface originating from one of the defects on the sample’s surface. The micro-crack has a width of about 3μm running across the surface that is not easily visible to the naked eyes(Figure 6.16c). Samples with surface defects generally had lower stresses and resulted in lower TL signals intensity values. The defects have lowered the stress level the composite can sustain thereby significantly reducing the energy in the system for the excitation of the TL crystals at failure.
6.2.5 Morphological Characterization with FESEM

The Ultramicrotome was used in preparing the surface of the ITOF cross-section (50:50 wt percent ZnS:Mn/epoxy) shown in Figure 6.17 before morphological characterization with the

Figure 6.16: a) ITOF sensor surface with fabrication defects, b) crack originating from surface defect, c) micro-crack on surface of the tested sample.

Figure 6.17: Scanning electron micrographs a) ZnS:Mn crystals b) cross-section of an ITOF sensor showing the ZnS:Mn crystals loaded coating, interface between the coating and the smooth-surfaced POF c) ITOF sensor coating with ZnS:Mn crystals randomly dispersed in the epoxy matrix d) void and crystal agglomeration in the ITOF coating.
FESEM. Figure 6.17a shows some of the ZnS:Mn crystals used in this study. The ITOF coating, the interface between the coating and POF, and the POF are shown in Figure 6.17b. The smooth morphology of the POF is easily distinguishable from the ZnS:Mn crystals-loaded ITOF coating.

The size of the interface (~2μm) between the coating and the POF permits effective side-coupling of TL emissions from the coating (vide infra) into the POF. The thin film coating of the ITOF made possible the placement of the TL crystals near to the surface of the transmission component (POF) for the successful coupling of the TL emissions into the POF. Effective side-coupling as evident by the high signal-to-noise ratio obtained from the tested samples makes distributed sensing with the ITOF possible when the entire length of the POF is coated with this TL thin film. The observed interface between the optical fiber and TL coating is not expected to adversely affect the structural integrity of a concrete structure because of its relatively small size.

As noted in Section 2.1.1, the interfacial transition zone (ITZ), between the hardened cement paste (hcp) and the aggregate, often has more voids and is weaker compared to the bulk cement matrix. The ITZ is about 30-50 microns wide [37] compared to the 2 microns for the ITOF interface.

In addition, the interface may actually be an advantage in that it isolates the TL coating (signal generating component) from the optical fiber (signal transmission component) of the ITOF sensor. If the sensor coating at any point along the optical fiber is damaged, there is greater chance of the transmission component being undamaged and its being able to transmit signals generated at other points along the optical fiber.

The ZnS:Mn crystals are randomly distributed in the epoxy matrix of the coating (Figure 6.17c). Except for a few larger ZnS:Mn crystals, the crystals are uniformly dispersed throughout the epoxy film giving it the capability to produce triboluminescent signals during impact, cracking or flexing. There are also voids and crystals agglomeration in the sensor coating as highlighted in Figure 6.17d. Crystal agglomeration further increases the randomness and variability in the TL responses from the sensors.
Figure 6.18: FESEM micrograph of fractured surface of ITOF (50:50 wt percent ZnS:Mn/epoxy) cross-section a) virtually all crystals in the fractured plane were fractured b) ZnS:Mn crystals with fractured surface showing fracture lines.

The fractured surfaces of the tested ITOF sensors (50:50 wt percent ZnS:Mn/epoxy) were also characterized using the FESEM. It can be seen that virtually all the crystals in the fractured plane were fractured as the crack propagated through them (Figure 6.18a). The fracture lines on the surfaces of the crystals can be clearly seen in Fig. 18b. This is an indication that a strong bond/interface exists between the ZnS:Mn crystals and the epoxy matrix. This allows effective load transfer on to the crystals to fracture them as the crack propagates through the epoxy matrix of the coating. The size of the interface is about 0.1μm. The fracturing of the crystals is also an indication that the dominant TL mechanism at work during the testing of these samples was fracto-triboluminescence.

Figure 6.19 shows the FESEM micrographs of the 60:40 (wt percent) ZnS:Mn/epoxy ITOF sensor coating. Compared to the micrographs of the 50:50 (wt percent) ZnS:Mn/epoxy ITOF (Figure 6.18), a weaker interface exists between the ZnS:Mn crystals and the epoxy matrix. The interface is about 0.5μm (Figure 6.19b) compared to about 0.1μm in the 50:50 (wt percent) ZnS:Mn/epoxy ITOF system. There are also more evidences of crystal pullouts (Figures 6.19a and 6.19b) as indicated by the many empty grooves on the fractured surface. Furthermore, the weak interface must have been responsible for the relatively low TL signal intensity values recorded in Figure 6.14.
Figure 6.19: FESEM micrographs of a) fractured surface of the 60:40 (wt percent) ZnS:Mn/epoxy ITOF sensor coating, b) close-up view showing grooves and many crystals not fractured because of weak interface in the composite system.

The weak interface resulted in ineffective load transfer on to the crystals resulting in significant reduction in the number of fractured crystals (Figure 6.19b) when compared to the 50:50 (wt percent) ZnS:Mn/epoxy ITOF system (Figure 6.18).

### 6.3 Conclusion

The TL behavior of two different types of ITOF sensor configurations namely the 50:50 and the 60:40 (wt percent) ZnS:Mn/epoxy systems under 3PBT loading have been studied. Characterization techniques such as Raman spectroscopy and Field emission scanning electron microscopy were used to further gain insights into the sensors’ behavior and properties. It has been shown that the ITOF is able to generate TL signals without the total fracturing of the coating. Development of internal micro-cracks is believed to be responsible for this because there was a loss in the load-carrying capacity of the tested sensors at failure. The sensor is also able to distinguish the nature of damage-causing event. It generated higher TL signal values with increase in the testing (load application rate) speed.

Furthermore, fabrication defects such as surface and hidden voids adversely affect the sensor’s performance. In addition, processing limitations discourage the use of ITOF sensors with higher ZnS:Mn wt ratio that exceed 50%. FESEM characterization indicates a stronger interface between the crystals and the polymer matrix in the 50:50 (wt percent) than in the 60:40 (wt...
percent) ZnS:Mn/epoxy systems. The stronger interface promotes effective load transfer resulting in higher TL signals. Hence, this study shows that the 50:50 (wt percent) ZnS:Mn/epoxy system is the preferred one for an ITOF sensor system. Finally, the TL property of the ZnS:Mn crystals were preserved in the ZnS:Mn/epoxy composite coating of the ITOF as indicated by the Raman characterization.
CHAPTER SEVEN

TRIBOLUMINESCENT
MULTIFUNCTIONAL CEMENTITIOUS COMPOSITES

The development of the ITOF sensor will make it possible to create multifunctional cementitious composites with *in-situ* damage detection capabilities. Such a system will mimic the human nervous system with the integrated ITOF sensors acting as the nerves with both sensing and signal transmission capabilities. Figure 7.1 is a schematic illustration of a triboluminescent multifunctional cementitious composite (TMCC) bridge girder with *in-situ* crack monitoring capabilities for protecting the steel reinforcement from corrosion through early crack detection.

Figure 7.1: Schematic of double layer sensor TMCC girder for early crack detection.

7.1 Materials and Methods

The materials, fabrication processes and experimental procedures for characterizing the damage monitoring capability of the ITOF sensor in the TMCC are described as follows.

7.1.1 Silicon Mold Fabrication

Silicon molds were fabricated for producing the TMCC beams. The silicon molds offer the advantages of:

1. Ease of incorporating the ITOF sensors
2. Ease of demolding the beams without damaging the incorporated ITOF sensors
3. Repeated use
Wooden molds were cut with an electric saw to the dimension of the desired TMCC beams. The surfaces of the beams were then smoothened with grades 320 and 600 carbide sandpaper. The surfaces were coated with wax to make them impervious. One of the larger surfaces of the wooden beams was not waxed so that the adhesive could be easily applied. Rectangular boxes (with no cover) were fabricated from acrylonitrile butadiene styrene (ABS) plastic. The ABS plastic was cut with a waterjet (by Omax Inc.) and the pieces joined with a fast cure epoxy adhesive. The prepared wooden beams were then fastened on to the base of the ABS box with a fast cure epoxy adhesive. The setup was then sprayed with 2500 mold release film to facilitate de-molding. The dimensions of wooden beam molds fabricated are 300 x 90 x 75mm.

The silicon molds were made using Polytek silicon two-part epoxy system. The two-part epoxy was prepared according to the manufacturer’s instruction and manually mixed thoroughly to ensure even dispersion. The mixture was then poured into the prepared ABS mold with the wooden molds and allowed to cure overnight before de-molding. Figure 7.2 is a schematic giving the dimensions (mm) and positioning of the wooden molds in the ABS mold before pouring of the silicone for the fabrication of the TMCC beams (300 x 90 x 75mm).

![Figure 7.2: Schematic of the dimensions (mm) and positioning of wooden molds in the ABS mold for silicon mold for fabricating TMCC beams (300 x 90 x 75mm).](image)
7.1.2 TMCC Fabrication
The mix design for the fabricated cementitious composite is as highlighted in Table 7.1. The appropriate constituents were measured and mixed thoroughly in an electric-powered concrete mixer (Figure 7.3).

Table 7.1: Constituents of triboluminescent multifunctional cementitious composite (mortar).

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Proportion to cement content (by wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement</td>
<td>1.000</td>
</tr>
<tr>
<td>Fly ash</td>
<td>0.300</td>
</tr>
<tr>
<td>Sand</td>
<td>3.575</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>0.012</td>
</tr>
<tr>
<td>Water</td>
<td>0.585</td>
</tr>
</tbody>
</table>

Figure 7.3: Mixing of TMCC constituents in an electric-driven concrete mixer.

After thorough mixing in the electric-driven concrete mixer, the CC mix was poured into prepared silicon molds. The molds were prepared by cleaning with water, drying with
pressurized air, coating with release agent (PVA or 2500) and allowing to dry. The ITOF sensors were then placed in the molds (Figure 7.4a) before pouring the CC mix (Figure 7.4b). The pouring was done in three phases with rod tapping at each phase to eliminate trapped air. The CC beams were de-molded after 24 hours and immersed in water in a curing basin at room temperature to cure usually for 28 days.

Figure 7.4: (a) Silicon mold with single layer ITOF sensor ready for CC pouring, (b) fabricated TMCC beams ready for de-molding from silicon mold.

Cylindrical samples for compression tests were also fabricated by using 3” x 6” (76.2 x 152.4mm) cylindrical plastic molds. Figure 7.5 shows some TMCC beams and CC cylinders in the curing bath. A day before testing, the TMCCs were removed from the curing basin and allowed to dry.

Figure 7.5: TMCC beams and CC cylinders being cured in a water bath.
7.1.3 Flexural Test
Three point bend tests (3PBT) were performed on the TMCC beams. A MTS 858 mechanical testing machine with 25 kN capacity was used. The TL signals generated by the TMCC during crack propagation were transmitted through the optical fibers to the photomultiplier tube (PMT) from Hamamatsu Corporation (H10722-01) where they were converted into electrical signals (voltage) and quantified. Some of the samples were instrumented with strain gages (by Kyowa Co, Japan) before being tested (Figure 7.6a). The 3 point bend test setup is as shown in Figure 7.6b. The strain readings were monitored and recorded with a Vishay P-35 strain gage meter with a data acquisition rate of 1 Hz. Morphological studies were conducted on some of the tested samples with a Field Emission Scanning Electron Microscope (JEOL JSM-7401F).

Figure 7.6: a) TMCC beams with strain gages installed b) Three point bend tests (3PBT) set up.

7.2 Results and Discussion
The results from this study are hereby presented and discussed.

7.2.1 Damage Characterization with TL Emission Profile Analysis
The TL emission profiles from the ITOF sensors at beam failure were analyzed to gain insights into the mechanism of the TL excitation of the ITOF sensor in the mortar beams. The analyses have been divided into two parts based on the location of the ITOF sensor relative to the neutral axis of the beam before loading which determines whether it is in the tension or compression zone during loading (Figure 7.7).
Figure 7.7: Location of ITOF relative to neutral axis determines whether it is in tension or compression zone during flexural test of cementitious beams.

**ITO Sensor Behavior in Tension Zone of Mortar Beams**

Figure 7.8a shows a typical TL signal obtained from the ITOF sensor during the brittle failure of the mortar system. The TL signal clearly depicts the catastrophic (sudden) failure associated with unreinforced cementitious composites. There were no alarming signals detected before the brittle failure of the beam. A closer look at the signal at higher magnification however revealed some interesting results (Figure 7.8b). The plot shows 3 distinct peaks in the TL emission profile. The three distinct TL emission peaks observed occurred in decreasing peak TL intensity values. The first emission had the largest TL peak value of 4.126V; the second had a value of 1.75V and the last had a value of 0.56V. The emission lasted for about 18.2ms.

The emission duration and the multiple peaks indicate that more than one emission took place during the fracturing of the sample. Earlier work by Hollerman et al [152] indicates that the TL emission of ZnS:Mn lasts for about 3ms and that ZnS:Mn is strongly triboluminescent with a prompt fluorescence decay time of about 300 µs [111, 152]. The fluorescence decay time is unique to each material and can be defined as the time needed to reduce the light intensity to $e^{-1}$ (36.8%) of its original value [152].
Figure 7.8: (a) Typical TL signal depicting brittle failure of unreinforced cementitious composite (mortar) beam, (b) Close-up view of TL signal showing multiple emissions over extended period.

Considering the expected duration of a single TL emission (~3ms), the observed total TL emission duration of ~18.2ms, and the observable TL peaks (3), there is a high probability of many more emissions that overlap, making some peaks indistinguishable such as highlighted by the dotted lines in Figure 7.8b. There tends to be an earlier emission whose peak overlapped with the main (first) emission peak observed in Figure 7.8b.

This postulation is reinforced in Figure 7.9a which is a close-up view of the TL signal from another sample. Three very distinct peaks can also be observed. However, unlike the previous sample, the first peak did not have the highest TL intensity value. The first peak had a TL
emission of about 0.3 V, the lowest of the three distinct peaks. The second has the highest TL intensity value of 1.08 V while the last peak has a value of 0.75 V. The TL emissions lasted for about 16.5ms. Figure 7.9b shows the fractured beam with the integrated ITOF sensor across which the crack also propagated.

Figure 7.9: a) TL signal shows multiple emissions as well as a small early TL emission peak suggestive of sensor excitation prior to actual contact with the crack (emission time ~16.5ms), b) Fracture plane cuts across ITOF sensor.

The TL profiles in Figure 7.8b and Figure 7.9a suggest the excitation of the ITOF sensor before the crack actually got in contact with the sensor. Evidence of the remote (non-contact) excitation of the ITOF sensor is illustrated in Figure 7.10. Figure 7.10(a) shows the TL signal obtained from a sample that fractured without the crack passing through the ITOF sensor while Figure 7.10b shows the fractured surface of the mortar beam without the crack passing through the integrated ITOF sensor. The fracture plane is about 10mm from the ITOF sensor. A comparatively smaller peak TL signal (0.11V compared to the least value of 0.79V) was obtained indicative of the sensor’s ability to sense damage some distance away from it. The emission duration was about 12ms.
Figure 7.10: a) TL signal due to remote damage sensing by ITOF sensor (emission time ∼13ms), b) Fractured mortar beam cross-section showing no ITOF sensor in fractured plane.

Figure 7.11 shows the TL signal (Figure 7.11a) and profile (Figure 7.11b) obtained from flexural test conducted directly on ITOF sensors with rectangular cross-section (∼3 x 3mm). The emission duration was about 3ms which is typical for ZnS:Mn crystals. This shows that the elongated emission duration experienced with the ITOF incorporated into the mortar system is as a result of the sensor sensing the crack propagation across the thickness of the beam.

The high speed of light ($3 \times 10^8$ m/s) suggests that the observed multiple emissions must be due to different excitation time of the randomly dispersed ZnS:Mn crystals in the ITOF coating as the crack propagated through the beam. The small coating thickness and high speed of light make it impractical to suggest that the multiple emissions detected was caused by time differences in signal coupling into the POF of the sensor because of the differences in the position of the randomly distributed ZnS:Mn crystals within the coating relative to the POF.
Figure 7.11: a) TL emission from flexural test on ITOF sensor, b) TL emission spectral with TL duration ~3ms.

Based on the preceding discussion, three modes of ITOF sensor excitation in the mortar beams have been identified (Figure 7.12). The first mode is pre-indirect excitation (Figure 7.12a and Figure 7.12a’) that occurs at the lower (tensile) side of the beam when the rapidly propagating crack is at some distance away from the integrated ITOF sensor in the beam. The second is the direct excitation mode that occurs when the crack comes in contact with the ITOF sensor (Figure 7.12b and Figure 7.12b’). The final mode is the post indirect excitation (Figure 7.12c and Figure 7.12c’) that occurs after the direct excitation, when the crack is moving away from the sensor position. This is evident by the reduction in the TL emission peak values as the crack moves away from the sensor location (Figure 7.12c’). We observed that the TL signal intensity (peak)
values for indirect excitations (Figure 7.12a and Figure 7.12c) are significantly lower than the TL signal values observed in direct excitation (Figure 7.12b).

Figure 7.12: Schematic of different modes of ITOF sensor excitation in mortar beams a) pre-indirect b) direct c) post-indirect excitations.

**ITOF Sensor Behavior in Compression Zone**

Figure 7.13 shows the TL emission profile obtained from an ITOF sensor located in the compression zone (above the neutral axis) of the mortar beam. The compressive load caused multiple signals to be generated because of the prolonged contact of the cracked surfaces.

Figure 7.13: TL profile from ITOF sensor located in compression zone of mortar beam.
compared to the quick separation experienced in the tension zone. Consequently, the total TL emission duration was about 60ms, which is more than twice that experienced by ITOF sensors in the tension zone (average TL emission of 28.84ms). In addition, there are more multiple peaks or emissions compared to that observed in ITOF sensors located in the tension zone. There were approximately 13 distinct peaks compared to an average of 4 peaks for ITOF sensors in the tension zone. This is an indication of multiple TL excitations of the ITOF crystals as evident by the multiple peaks and the prolonged TL emission duration. In addition, the maximum TL peak value obtained (0.134 V) in the compression zone was significantly lower than that obtained in samples where the ITOF was located in the tension zone (with the least peak value of 0.79 V).

The multiple peaks and longer emission duration can be explained by the position of the ITOF relative to the neutral axis. The ITOF signal was located approximately 5 mm above the neutral axis. This means the sensor was in compression. When crack initially occurred at the base of the sample, TL signals were generated in the sensor even though the crack had not yet propagated to the ITOF sensor (pre-indirect excitation). The ITOF sensor is believed to have been excited by the energy released during the creation of the fractured surfaces as the crack propagated through the host structure. As the crack travels up the sample and more energy is released, the sensor continues to emit TL signals until the crack reaches the sensor. At that point, the maximum peak TL signal is observed (direct excitation). This maximum peak TL signal is much lower than that for tension because the load on the ITOF sensor is in compression and may not necessarily result in the cracking of the ITOF coating as may be the case with the sensor in tension. Moreover, when cracking occurs, the failure mode is not as violent as that experienced under tension. The fracturing of the coating usually leads to the generation of much higher TL intensity values because of fracto-triboluminescence.

The sensor will continue to emit TL signals as the crack continues to propagate up the sample away from the sensor location. The compression state of the system tends to slow down the crack propagation as evidenced by the prolonged and multiple peaks (emissions) after the maximum signal. The sensor is able to sense the crack propagation for an extended period. From the above, it is possible to gain insight into the loading condition within a structure, whether it is in tension or compression, from an analysis of the TL profile generated from the integrated ITOF sensor. A thorough understanding of the underlying mechanisms responsible for the different TL profiles
and how they relate to damage characterization is needed before successful field deployment of the ITOF sensors. This is subject to further research work.

7.2.2 Real-time Damage Monitoring in Mortar Beams
All of the over 20 samples tested, gave TL signals at the instance of brittle failure. The typical responses obtained at the instance of failure of the unreinforced cementitious beams are as shown in (Figures 7.15 and 7.16). To validate the effectiveness of the ITOF sensor to provide in-situ and real time damage monitoring in cementitious composites, four TMCC beams were instrumented with strain gages as shown earlier in Figure 7.6. Damage was successfully detected in real time as can be seen by the coinciding of the time when the TL signal was detected with the time the sample failed as indicated by the loss in the load carrying capacity (Figure 7.14).

Figure 7.14: TL signal at instant of brittle failure of unreinforced mortar beam.
Figure 7.15: Large increases in strain value at instance of brittle failure corresponding to instance of TL signal generation.

Similarly, the strain gage experienced a sudden increase in the strain value due to crack opening at the instance of brittle failure of the beam (Figure 7.15). At the same instance, a jump in the TL signal was observed (Figure 7.15). Unlike the ITOF sensor, a crack must come in contact with the strain gage before it can detect it. The ITOF sensor however offers the superior advantages of distributed and non-contact sensing as demonstrated earlier.

### 7.2.3 Triboluminescent Peak Intensity

The TL intensity signal values were plotted against the stress at failure for the different TMCC beams tested under 3PBT. A poor correlation exists between the TL peak intensity values and the stress at failure of the beams (Figure 7.16), and the ITOF stress at failure (Figure 7.17). Both stresses were calculated based on the linear elastic beam theory. The result shows that the linear elastic beam theory is not adequate to describe the mortar beam system studied. The assumptions that the beam is perfectly homogeneous and isotropic, i.e. of the same density and elastic properties throughout are violated by the highly heterogeneous mortar beam system. This may be responsible for the scatter or poor correlation between the stress levels and the TL intensity values. It is also an indication that the TL intensity, though an indicator that damage has occurred or is underway, needs to be combined with the TL profile analysis described earlier for effective damage characterization in structures.
Another important consideration is the test configuration. The 3PBT loading condition coupled with the fact that the beams were unreinforced suggests a very high probability of the fracturing of the ITOF coating during the flexural tests. Figure 7.18 shows the typical large crack observed during the testing of the samples. The crack widths that could well exceed 2mm and the sudden caving in of the two fractured surfaces definitely promote the fracturing of the coating.
Earlier work on the ITOF sensor have shown that whenever the coating fractures, the ZnS:Mn crystals within it also fracture as highlighted in the repeated SEM micrograph from Chapter 6 (Figure 7.19). This implies that fracto-triboluminescence is the prevailing TL phenomenon in action. Fracto-TL is luminescence produced due to the creation of new surfaces during the fracture of solids [21]. During fracto-TL, there is creation of charged surfaces at fracture due to processes such as piezoelectrification, movements of charged dislocations, and charged defect barodiffusion [22, 139]. The surface charges are neutralized by charge carriers or ions produced from the dielectric breakdown of the intervening gases and solids.

The peak TL intensity $I_m$ resulting from Fracto-TL of ZnS:Mn crystal is however dependent on the charge density $\gamma$, area of the fractured surfaces $A$, luminescence efficiency associated with the movement of carriers produced by the dielectric breakdown of the crystals $\eta$, and rate constant for the relaxation of charges on the newly created surfaces $\alpha$ as stated in Eqn 2.22. Since $A = 2WH$ is the area of the newly created surfaces where $H$ is the thickness of the crystal cleaved along a plane parallel to its width $W$, Eqn (2.22) implies that $I_m$ should increase linearly with $A$ and $\gamma$. This is contrary to the case of elastico-triboluminescence where the TL peak intensity is a function of the applied stress. It may be desirable to have the ITOF sensor operate within the elastico-TL range that does not involve the fracturing of the coating. This should be
possible with reinforced cementitious composite systems which is the targeted structures for the ITOF sensor system.

\[ I_m = \eta \alpha A \] (2.22)

Figure 7.19: a) Fractured surface of ITOF cross-section showing fractured ZnS:Mn crystals in epoxy matrix b) fracture lines on the surfaces of the fractured crystals.

**Comparison of Failure Stresses from Flexural Characterization of Unreinforced Cementitious Composite (TMCC) Beam and Direct Loading of the ITOF**

Figure 7.20a shows the stress at failure and the corresponding TL peak signal obtained from 5 different rectangular-shaped ITOF sensor tested under 3PBT condition (Figure 7.20b). The sensors’ dimensions (~3 x 3 x 50mm) were similar to the ITOF sensor used in the mortar beams used in this study. All the samples were tested to failure resulting in their fracture. The maximum stresses recorded at failure were well below the 100MPa required for fracto-TL in literature but was significantly higher than that obtained during the failure of the mortar beams. Localized stress concentration due to defects such as cracks might have caused the localized stresses around the crystals to reach the 100MPa level required for fracto-TL during the direct flexural loading of the ITOF. The significant differences between the failure stress levels for the direct flexural loading of the ITOF and that of the mortar beams suggest that the fracto-TL emissions observed in the TMCC (mortar beams) are not related to or caused by the failure stresses on the mortar beams.
The fracturing of the ITOF coating and consequently of the crystals is most likely to have been due to the bending of the integrated ITOF sensor when the beam cracked and the two newly created sections bent because the beams were not reinforced.

7.3 Summary

Triboluminescent multifunctional cementitious composites consisting of integrated ITOF sensors with \textit{in-situ} crack monitoring capabilities have been successfully fabricated and demonstrated. A new approach to damage characterization by triboluminescent (TL) emission profile analysis was also introduced. TL profile analysis indicates that the ITOF sensor in a TMCC is able to detect rapid crack propagation through unreinforced cementitious composite beams. The TL emission profile may also provide insights into the loading state of the structure based on sensor location (tension versus compression behavior of structure). While the TL intensity signal provides an indication of the occurrence and magnitude of damage, the TL profile analysis promises to facilitate better understanding of crack propagation in composite structural materials.
CHAPTER EIGHT

CONCLUSIONS

The main conclusions and contributions from this work are hereby presented. In addition, opportunities for future work are discussed.

8.1 Conclusions

The following conclusions can be drawn from this work:

1. The problem of triboluminescent emissions detection and transmission in opaque composite materials as stated in Section 1.2 was successfully solved through the development of the ITOF sensor (Chapter 4). Triboluminescent-based real-time damage monitoring is possible in opaque structures as demonstrated by the triboluminescent multifunctional cementitious composite beams that were fabricated (Chapter 7).

2. Triboluminescent damage sensing by the direct dispersion of TL crystals in cementitious composites has been shown feasible (Chapter 3). This study has shown that a ZnS:Mn concentration by weight percent of 10% gives enhanced TL responses (high signal to noise ratio) without adversely affecting the mechanical properties of the host structure. The dense network of optical fibers that would be required for the successful transmission of TL emissions from the randomly distributed TL crystals however greatly limits the practicality of this approach.

3. The ITOF sensor is expected to have no adverse effect on the host cementitious composite structure because the ZnS:Mn crystals are not directly dispersed within the host material. As shown in Section 4.4.2, the ZnS:Mn crystals did not adversely affect the thermo-mechanical properties of the ITOF sensor coating. Furthermore, smaller ITOF sensor diameter and higher TL crystal content (by weight fraction) have been shown to exhibit higher TL signal values (higher signal to noise ratios) when damage events like crack and impact occur. Fabrication limitations however currently limit the ZnS:Mn content (by weight fraction) to 0.5 of the ZnS:Mn/epoxy of the ITOF coating thin film.

4. Efficient side-coupling of TL signals into polymer optical fiber is possible as demonstrated by the ITOF sensor. By locating the source of the TL signals near the surface of the polymer optical fiber, enhanced side-coupling can be achieved. This has been demonstrated in the ITOF sensor where the randomly dispersed TL sources
(ZnS:Mn crystals) are located near the surface of the POF by the thin film of the ITOF coating. Enhanced side-coupling of TL signals from the thin film coating makes truly distributed sensing possible along the coated length of an ITOF sensor. For effective damage characterization, it is important that both ends of an ITOF sensor are connected to a photodetector. This will ensure that all the TL emissions coupled into the POF are captured. Experimental work has shown that there is a random and uneven distribution of the TL emissions between the two ends of the sensor when damage events occur.

5. Analysis of the TL emission profile from tested unreinforced triboluminescent multifunctional cementitious composites reveals three modes of excitation of the integrated ITOF sensor. The TL profile analysis further showed that the sensor is able to detect crack propagation within the TMCC even when the crack is not in contact with it. Based on the TL profile analysis, the ITOF sensor in a TMCC can act as a dynamic crack sensor that monitors crack propagation within the structure in which it is integrated as demonstrated in Section 7.2.2.

6. The ITOF impact excitation model attempts to predict the TL responses of the ITOF sensor as a function of the applied impact energy within the elastico-triboluminescence limit, the sensor’s diameter and the TL crystal volume fraction of the sensor coating. Uneven dispersion of the ZnS:Mn crystals within the sensor coating coupled with non-uniform coating diameter resulted in high variability in the TL responses of the sensors under impact loading. Consequently, the model could not be validated.

8.2 Summary of Contributions

A summary of my contributions is as follows:

1. This work investigated and harnessed the triboluminescent properties of ZnS:Mn for real-time damage sensing in cementitious composites (CC). This is the first known utilization of the triboluminescence phenomenon in this host material system. I have demonstrated the viability of TL-based sensors in CC by using two different approaches: direct dispersion of TL crystals in the host structure, and development of the in-situ triboluminescent optical fiber (ITOF) sensor.

2. Triboluminescent-based sensing of mortar systems with direct dispersion of ZnS:Mn crystals was studied. The effects of different TL crystals content levels (weight fraction)
on the triboluminescent response as well as on the mechanical properties of the mortar system were studied. The TL crystals content level (weight fraction) that give enhanced damage sensing behavior without adversely affecting the mechanical properties of the host CC structure was determined.

3. The problem of TL signal transmission in opaque structures was addressed by developing the bio-inspired *in-situ* triboluminescent optical fiber (ITOF) sensor with integrated sensing and transmitting components. A patent application for the sensor has already been submitted to the US Patent Office. The fabrication process for the sensor was developed and key sensor design parameters for enhanced sensor performance (higher TL signal values) were investigated. It has been established that thinner coating and higher TL crystal content result in sensors with enhanced triboluminescent performance (higher-signal-to-noise ratio).

4. Effective side-coupling of TL signals into polymer optical fiber has been demonstrated. This was accomplished by using triboluminescent thin films. The thin films help to position TL crystals close to the surface of the POF resulting in enhanced coupling of the TL emissions into the POF. This approach makes the development of truly distributed sensors feasible when the entire length of the POF is coated with the TL thin film.

5. The properties of the TL thin film of the ITOF sensor were characterized by using characterization techniques such as Raman spectroscopy, FESEM and DMA. This provided important insights on the effect of the fabrication process and ZnS:Mn/epoxy interactions on the TL properties of the ZnS:Mn crystals; and the effects of the ZnS:Mn content (weight fraction) on the thermo-mechanical properties (glass transition and storage modulus) of the ITOF sensor coating. FESEM analysis provided insights on the interfaces and the failure mechanism of the TL crystals in the TL thin film of the sensor.

6. Triboluminescent damage sensing behavior of the ITOF sensor under direct flexural loading was also studied. It has been shown that a strong bonding exists between the ZnS:Mn crystals and the epoxy matrix of the sensor coating in the 0.5 (weight fraction) ZnS:Mn/epoxy coating of the sensor. Consequently, the fracture of the coating results in the fracture of the ZnS:Mn crystals thereby making fracto-TL the predominant TL
mechanism at work. Such strong bonding could not be developed in the 0.6 (weight fraction) ZnS:Mn/epoxy sensors with the current fabrication process.

7. Triboluminescent multifunctional cementitious composites (TMCC) with in-situ and real-time damage monitoring capabilities were developed by integrating the ITOF sensor into mortar beams during fabrication. The damage monitoring behavior of the TMCC was studied under flexural loading. Evidences were provided why the correlation of TL intensity values and failure stress (global estimate) of a TMCC will not adequately describe the crack propagation (a local phenomenon) in the unreinforced TMCC.

8. While virtually all TL-based sensing work had focused on the use of the TL emission intensity for damage characterization, a new approach to damage characterization that is based on the analysis of the TL emission profile was introduced in this work. TL emission profile analysis indicates that the ITOF sensor senses crack propagation through the TMCC beam. Three modes of sensor excitation were observed and reported. This new approach promises to facilitate the understanding of crack propagation in composite materials subject to further work.

8.3 Future Research

This work on the application of the triboluminescence phenomenon for damage monitoring in cementitious composites has created many new opportunities for highly rewarding research work. Future research work includes:

1. Damage characterization of ITOF sensor behavior in reinforced cementitious composites:
   The current research work had focused on the damage characterization of the ITOF sensor in unreinforced cementitious composites. Characterization of the ITOF sensor’s performance in reinforced composites is therefore needed. For practical application of the ITOF sensor, it needs to be integrated in reinforced systems such as steel reinforced and fiber reinforced concrete. The damage monitoring behavior of the sensor in such systems needs to be characterized. This will enhance the understanding of the sensor behavior and gradual crack propagation in reinforced systems. It is also important to characterize the behavior of the sensor in TMCC under different loading conditions such as fatigue and impact loading.
2. **TL emission profile analysis:** As noted in Section 7.2.1, further work is needed to gain a better understanding of the TL emission profile before it can be effectively used for damage characterization. Of particular importance is the TL emission profile analysis of reinforced TMCC. It is important to be able to determine the crack distance away from the sensor from which remote sensing can occur. This knowledge will play a critical role in the successful implementation of the ITOF in engineering structures. Effective theoretical and empirical models need to be developed also as highlighted in Section 5.3.

3. **Improved fabrication approach and model development:** The problems of TL crystals dispersion and non-uniformity of coating have to be solved for more consistent sensor responses. Furthermore, the TL intensity depends on a large number of factors, including stress, strain, strain rate, pressing rate, temperature, atmospheric pressure, dielectric constant, mobility, particle/crystal, sample mass, trap depth, piezoelectric constant, trap concentration, radiation fluence, dopant type and concentration, sample firing temperature, sample sintering temperature, sample annealing temperature, firing time, sintering time, charge carrier capture cross section, number of successive pressings, efficiency for the conversion of mechanical energy into light energy, crystal structure, crystallographic direction, piezoelectric constant, dislocation density, area of newly created surfaces, dislocation charge, sample hardness, and sample age [162]. Consequently, the exact cause of TL is unknown [112, 162, 163] and subject to further investigation.

4. **Application of ITOF sensor as externally bonded sensor system:** With the large number of aged civil infrastructure systems like bridges, a critical application opportunity for the ITOF sensor is on existing bridges. There is the need to develop installation methods for external bonding of the ITOF on to engineering structures, and to characterize the damage monitoring behavior of such externally bonded ITOF. This work only focused on ITOF-integrated composites.

5. **Techniques for determining damage location:** The ITOF sensor has the capability to monitor damage along its coated length. Techniques to determine the location along the length of the sensor from which the TL signal originates need to be developed. This will make damage location to be readily determined.
6. **Durability tests on the ITOF sensor**: Civil infrastructure systems like bridges are designed to last for a very long time, often exceeding 50 years. The long-term effects of ITOF sensor’s exposure to different environmental factors such as concrete’s high alkaline environment need to be studied.
APPENDIX A

LIST OF PUBLICATIONS

PEER-REVIEWED JOURNAL ARTICLES

Published


4. M. J. Uddim, T.J. Dickens, J. Yan, R. Chirayath, D.O. Olawale and O.I. Okoli. “Solid state dye-sensitized photovoltaic micro-wires (DSPMs) with carbon nanotubes yarns as counter electrode: Synthesis and characterization” Solar Energy Materials and Solar Cells 2013, 108, 65-69. The paper describes the development and characterization of an innovative all solid state dye sensitized photovoltaic micro-wires (DSPMs) using low-cost, thermally-stable and highly conductive titanium micro-wires and carbon nanotubes yarns (CNYs). Highly inter-aligned, ultra-strong and flexible CNYs with excellent electrical conductivity, mechanical integrity and catalytic property were successfully used as counter electrodes (CEs).
5. **D. O. Olawale**, M. J. Uddin, K. Kliewer, T. J. Dickens and O. I. Okoli. “Triboluminescent optical nerve for real-time damage monitoring in composites” Smart materials and structures. The article reports on the fabrication of the triboluminescent multifunctional cementitious composites with in-situ damage monitoring capability. A new approach to damage characterization based on triboluminescent emission profile analysis was also presented.


*In preparation*

7. **D. O. Olawale**, M. J. Uddin, K. Kliewer, T. J. Dickens and O. I. Okoli. “Characterization of ZnS:Mn-epoxy thin film for in-situ damage monitoring in composite structures” Structural health monitoring. The paper will report results from various characterization techniques used to gain insight into the properties of the ZnS:Mn-epoxy thin film coating of the in-situ triboluminescent optical fiber sensor. The damage sensing behavior of the sensor under flexural loading will also be reported.


**CONFERENCE PROCEEDINGS**


PATENT

Triboluminescent Optical Fiber Sensor, U.S. Application No. 13/656,246
REFERENCES


BIOGRAPHICAL SKETCH

David O. Olawale received his B.Sc (Mechanical Engineering) from Obafemi Awolowo University, Nigeria in 2000 and his M.Sc (Industrial and Production Engineering) from the University of Ibadan, Nigeria in 2004. He taught at Covenant University, a leading private university in Nigeria, from October 2005 to August 2007 before proceeding to Florida State University for his doctoral studies in the Department of Industrial and Manufacturing Engineering. At FSU, his research focused on the development of triboluminescence multifunctional cementitious composites (TMCC). These are cementitious composites with both structural and in-situ damage monitoring capabilities. They will provide our civil infrastructure systems like bridges and dams with real time damage monitoring capability similar to that found in biological systems.

His research work has led to the filing of a patent application, publishing of journal articles and presentation of conference papers. The technology is also on the path to commercialization. It won 2nd place position in the highly competitive INOLEvation business plan competition (2012) organized by the Jim Moran Institute for Global Entrepreneurship.

Furthermore, during his doctoral studies, the author carried out leadership and administrative responsibilities such as being the Assistant Coordinator for both the NSF-sponsored research experience for undergraduate (RETREAT) program and the Air Force Research Laboratory sponsored internship (DREAM) program. He also served as the Coordinator for the Alumni Village Task Force that sees to the welfare of international scholars and their families from over 60 countries resident at the FSU Alumni Village housing facility.