CHAPTER 3

MECHANICAL PROPERTIES OF SWCNT-LEAD SILICATE GLASS COMPOSITE: EFFECTS OF SINGLE INDENTATION
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GLASS COMPOSITE: EFFECTS OF SINGLE INDENTATION

3.1 Introduction: Carbon nanotubes (CNTs) have been used as a prospective material for the fabrication of numerous advanced and multifunctional composites ever since its discovery in 1991 by S. Iijhima [1]. Among various properties of CNTs, especially the mechanical property of the carbon nanotubes was extensively explored in different host materials. The effort of utilizing the nanotubes as efficient reinforcing filler was initiated at the early part of this decade where some fruitful effects were studied on several CNT composites [2-5]. Looking for some lightweight and mechanically strong material in different applications, many researchers pay their attention towards the CNT incorporated composites where mostly polymers or metals were used as host materials [6-10]. Moreover, CNT-composites can also be considered as efficient materials for the tribological and the damping applications [11, 12]. In particular, CNTs were incorporated in the brittle materials like glass or ceramics to enhance the hardness, toughness and other important mechanical properties of the host matrix. However, overall enrichment of the mechanical properties in those composites was still a distant dream for the researchers. Usually it was observed that all mechanical parameters were decreased compare to the base glass, otherwise hardness was almost same where the toughness was enhanced in the composite [13, 14]. In chapter-2 it was shown that there was an overall improvement in the mechanical properties of SWCNT-borosilicate glass composite where the material was suggested as a potential object for different structural applications. Significant mechanical properties like hardness, fracture toughness, recovery resistance etc. were enhanced in SWCNT-borosilicate glass composite compared to the borosilicate glass. The embedded nanotubes played a vital role in regulating the various mechanical parameters where detailed clarification was given for the effects of SWCNTs in the composite. In this context the SWCNT induced cushioning behavior and
incremented localized plastic flow were discussed to understand the fundamental physics behind the improvement of the mechanical properties. However, it is interesting to observe the effects of the single wall carbon nanotubes in a different glass host by the same manner such that one can established the methodology as an effective pathway for the fabrication of CNT-glass composite. Considering the above scenario the study was further extended in the SWCNT incorporated lead silicate glass composite which is thoroughly investigated in this chapter. The same mechanical parameters were evaluated for this composite and it was also observed whether the base glass has any effects on those parameters or not. The behavior of entangled SWCNT bundles and the energy release from the strained nanotubes were revisited in this purpose. The basic intention of this work is to verify the effectiveness of the melt-quench route by which the composite was fabricated such that this material can also be utilized in air and space craft [15] and in different structural appliances [16].

3.2 Materials and methods:

3.2.1 Fabrication of SWCNT-lead silicate glass composite: 90% pure SWCNTs were purchased from Arry, Germany having length: 5-20 μm, OD: 1-2 nm and thermal conductivity ~ 4000 W/mK. For the dispersion of the nanotubes a mixture of aniline and toluene was selected where 0.1 gm of SWCNTs have been taken within the mixture of the organic solution. The detailed technique of this dispersion method was thoroughly discussed in chapter-2. In this work, the lead silicate glass was chosen as a host material with the following composition: SiO₂-52.7%, PbO-35.1%, K₂O-10.1%, Na₂O-0.5%, BaO-0.9%, As₂O₃-0.3%, and Sb₂O₃ -0.4%. Repeated survey of the temperature profile of this glass shows that the glass transition temperature (T_g) and the softening point are 560°C and 650°C respectively. After precise determination of the above factors the prepared SWCNT solution was properly mixed with some small pieces of the glass having weight ~4.2 gm. The wetted
glass frits were placed in an atmospheric controlled furnace and melted at 720 °C - 740 °C for 1 hour at Argon atmosphere. The melted material was then rapidly cooled to room temperature to avoid the crystal phases in the composite.

3.2.2 Polishing and Annealing: Some suitable pieces of the base glasses and the composites were optically polished by fine powders of different grain sizes. To make the samples stress free those were placed into an annealing furnace. The samples were heated and cooled within the furnace where the annealing temperature was 250 °C and the duration of the soaking time was 1 hour for all the samples.

3.2.3 Measurements of mechanical properties: Different mechanical properties of the lead silicate glass and the SWCNT-lead silicate glass composite were mainly evaluated by the micro indentation technique using Vickers’ indentation. Very fine powders were used for the three stage optical polishing of the specimens such that one can clearly observe the indentation impression through the objective of the microscope. Vickers’ micro indentation was carried out on those polished samples with loads 0.1N, 0.15N, 0.2N, 0.25N, 0.5N and 1N to determine various mechanical parameters of the base glass and the composite. For this purpose, Leco LH 700 micro indenter (shown in figure-5 of chapter-2) was used together with a Knoop indenter. Here the knoop indenter was only utilized for the determination of the Young’s modulus of the specimens. The fracture toughness of the materials was first calculated by the Direct Crack Method (DCM) and then also evaluated by the SEVNB technique through the three point bending test. In this case the ASTM standards have been followed regarding the dimension of the samples.

3.2.4 High resolution transmission electron microscopy: Among the various electron microscopy techniques HRTEM is the most essential method by which one can analyze the interior part of a specimen. By this method, the presence of SWCNTs inside the composite
material can be verified from the images. Moreover, the overall arrangement of the SWCNT bundles in the glass matrix can also be observed by HRTEM. The condition of the individual carbon nanotubes inside a bundle and the interaction of the nanotubes with the base material were further investigated in this context. The basic focus of this study was to ascertain whether the SWCNTs were well inside the glass host and to observe the subsequent situation of the nanotubes in the composite. Detailed analysis regarding the sample preparation for the HRTEM was discussed in chapter-2.

3.2.5 Field emission scanning electron microscopy: This microscopical method was mostly effective to determine the surface morphology of a material where the distribution of ingredients was clearly observed all through the composite material. Here, the indentation impressions along with the crack profile of all the specimens were thoroughly examined. Moreover, the distribution of the nanotubes inside the composite can be verified through this method where the interaction of the nanotubes with the crack profile was subsequently analyzed. The sample preparation technique for the FESEM was stated previously in chapter-2. In true sense, this particular study revealed as most significant characterization for this composite considering the following issues like indentation impressions, crack bridging, crack arresting etc.

3.3 Results and Discussions:

3.3.1 Hardness: The Vickers’ micro hardness ($H_v$) of the lead silicate glass and the SWCNT-lead silicate glass composite were evaluated by equation (1) where ‘$P$’ denotes the

$$H_v = 1.8544 \left( \frac{P}{d^2} \right)$$  \hspace{1cm} (1)
applied load on the specimens and ‘d’ is the diagonal length of the indentation impression for the corresponding load. The variation of the hardness with load is shown in figure-1 where one can observe that the hardness was increased with increasing load to a certain limit and then achieved a constant value with respect to the applied loads. The base glass together with the composite shows the same nature where the constant hardness started at 0.2N load for both the materials. The rise in the hardness value at the lower load region is the characteristic of the Reverse Indentation Size Effect (RISE) [17, 18]. The HV values below 0.2N load are termed as the apparent hardness or the surface hardness whereas the hardness above this limit represents the true hardness of the specimens. In this context, Meyer’s law can be analyzed (equation-2) and log P was plotted against log d (figure-2) to determine the Meyer’s exponent (n) for the base glass and the composite. Table-1 represents the linear regression analysis where the composite shows higher ‘n’ value compared to the base glass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>logA</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSG</td>
<td>3.74</td>
<td>2.24</td>
<td>0.997</td>
</tr>
<tr>
<td>LSCNT</td>
<td>4.01</td>
<td>2.33</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Moreover, it can be also observed from figure-1 that the composite exhibits enhanced hardness value than that of the base glass for all loads and almost 31% increment was observed in the HV value of the composite compared to the base glass at 1N load. In order to explain the higher hardness in the composite one can consider the successive FESEM images as shown in figure-3 and 4. The surface scanning picture of a non indented composite was exposed in figure-3 where it can be observed that the SWCNT bundles were entangled with each other and randomly distributed throughout the composite.
Figure-1: Hardness vs. load graph of lead silicate glass and SWCNT-lead silicate glass composite.
Figure-2: logP vs. logd plot for lead silicate glass and SWCNT-lead silicate glass composite.
Figure-3: FESEM image of the non indented zone of the composite shows random distribution of SWCNT bundles throughout the material; inset shows the entanglement of SWCNT bundles.
Figure-4: FESEM image of the indentation zone of the composite where entangled SWCNT bundles were present.
At this point one can think about the resilient nature of the nanotube bundles where they act as high pressure cushion in the composite material. Considering the FESEM image of an indented specimen as shown in figure-4, where one can see the interactions of the entangled SWCNT bundles with the indentation zone. This SWCNT bundles give rise to a cushioning behavior while interacting with the indenter and thereby reduces the indentation diagonal length in the composite once the applied load was withdrawn. Similar behavior was observed in SWCNT- borosilicate glass composite as discussed in chapter-2. In addition, Liu et al. [19] has described the cushioning performance of the highly resilient CNT agglomerates and correlating this behavior with the applied stress field. Furthermore, the super flexible character of the entangled and agglomerated carbon nanotubes was analyzed by different researchers [20, 21]. Therefore considering the above discussions it is clear that the cushion-like behavior of the entangled SWCNT bundles is the prime reason for the enhanced hardness of the SWCNT-lead silicate glass composite.

3.3.2 Young’s modulus: Knoop micro indentation technique was employed to determine the Young’s modulus (E) of the specimens as suggested by Marshall et al. (equation-3) in their report [22]. The following equation was used for this purpose where ‘H_K’, ‘b’ and ‘a’ were the knoop micro hardness, shorter diagonal length and the longer diagonal length measured at the time of indentation. The E values of the lead silicate glass and the SWCNT-lead silicate glass composite were found to be 50.01 GPa and 58.07 GPa respectively calculated at 1N load. Finally one can observe a small increment of Young’s modulus in the composite which is due to the presence of the SWCNTs in that material.
3.3.3 Fracture toughness: The fracture toughness ($K_{IC}$) of a material indicates the actual limit beyond which unstable crack propagation occurs. Here two different methods were employed to determine this parameter namely the Direct Crack Method (DCM) and the Single Edge V Notched Beam Technique (SEVNB) for all the specimens. In the first method the $K_{IC}$ values were determined by the equation (4) and found to be 0.49 MPam$^{1/2}$ and 0.62 MPam$^{1/2}$ at 1N load for the lead silicate glass and the SWCNT- lead silicate glass composite respectively. In equation (4) ‘E’, ‘Hv’, and ‘P’ denotes the same quantity as stated in previous discussion whereas C is the average crack length for the indentation at 1N load.

$$K_{ic} = 0.016 \frac{E}{H_v} \frac{P}{C^{1/2}}$$  \hspace{1cm} (4)

$$K_{ic} = g \frac{P_{f} I_0 10^{-6}}{B W^{3/2}} \left[ \frac{3(a/W)^{1/2}}{2(1-a/W)^{1/2}} \right]$$ \hspace{1cm} (5)

Where,

$$g = 1.9472 - 5.0247(a/W) + 11.8954(a/W)^2 - 18.0635(a/W)^3 + 14.5986(a/W)^4 - 4.6896(a/W)^5$$

Moreover, by the help of equation (5) one can evaluate the $K_{IC}$ values by the SEVNB technique where the fracture loads of the specimens were measured by three point flexure test. In this equation $P_{f}$, $L_0$, B, a and W were the experimentally measured fracture load, span length, specimen width, notch depth and specimen depth respectively. In this method the $K_{IC}$ values were found to be 0.64 MPam$^{1/2}$ and 0.91 MPam$^{1/2}$ for the base glass and the composite respectively. To verify the reproducibility of the absolute values the procedure was repeated on the same material and the reported values were the averages of five independent tests for all the materials. It was observed that the absolute $K_{IC}$ values differ in DCM and SEVNB technique whereas the increment of this parameter in the composite was almost 27% for both the procedures compared to the corresponding $K_{IC}$ values obtained in
the base glass. In this perspective different micrographical analysis become essential to find out the reason behind the increment of the $K_{IC}$ value in the composite. Actually the crack propagation was significantly obstructed by the SWCNT bundles which effectively shortened the crack length and make the foundation of the enhanced $K_{IC}$ value in the composite. Figure-5 shows the indentation impressions along with their crack profile where reduced crack length was observed in the composite compared to the base glass. Much closer view in and around the crack zone revealed the fact that somewhere the crack paths were repaired by the SWCNT bundles by making bridges inside the crack (figure-6a). In another view one can observe the crack was arrested by the accumulation of the SWCNT bundles around the path of the crack as shown in figure-6b. From this viewpoint it can be considered the work of D.G. Holloway [23] where he reported that the fracture process in glass was not ideally brittle and a plastic flow was always associated with the crack propagation. Hence both the materials (base glass and composite) contain a local plastic flow around the indentation crack zone. In addition the composite exhibits another type of energy dissipation emancipating from the SWCNT bundles located at the near vicinity of the indentation crack. For the precise understanding of this event the nanotube bundles were further investigated under HRTEM to ascertain the actual condition of the individual nanotubes (figure-7). The circles in that figure clearly show the straight and the curved segments of the SWCNTs within a bundle. This observable fact gives the evidence of the strenuous condition inside a bundle where the individual nanotubes were compelled into the glass host by means of the rapid quenching process during fabrication. So, a high amount of energy was released from those strained SWCNT bundles when a load was applied on the composite material. These types of energy dissipation from the curved SWCNTs under a stress field were discussed by Yakoboson et al. [24] and Pathak et al. [25]. Considering the
Figure-5: FESEM images of the micro indentation at 1N load for (a) lead silicate glass & (b) SWCNT lead silicate glass composite.
Figure-6: FESEM images of the crack zone in composite; (a) crack bridging & (b) accumulation of SWCNT bundles around the crack.
Figure-7: HRTEM image of the composite showing the individual nanotubes inside a bundle.
above arguments it can be stated that those emitted energies from the SWCNT bundles effectively increase the plastic flow around the pathway of the crack zone and drag the bundles towards the crack. The accumulation of the SWCNT bundles in and around the crack hinders the crack velocity and reduced the crack length in the composite. This type of crack arresting by the SWCNT bundles was observed in the case of SWCNT-borosilicate glass composite as described in chapter-2.

3.3.4 Reduced Young’s modulus: A test material and the indenter tip both were elastically deformed at the time of indentation which was estimated by the Reduced Young’s Modulus ($E_r$) of the material. Regarding the values of the Young’s modulus and the Poisson’s ratio for the specimen and the indenter one can easily determined the $E_r$ values of the specimens

\[
\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i}
\]

by equation (6). Here $E$, $v$ and $E_i$, $v_i$ are respectively denoted the Young’s modulus and the Poisson’s ratio of the indenter and the test specimen. In this case evaluated $E_r$ values were 49.82 GPa and 57.45 GPa for the lead silicate glass and the SWCNT-lead silicate glass composite respectively. Hence one can observe the incremented $E_r$ value in the composite than that of the base glass due to the presence of SWCNTs in the composite material.

3.3.5 Recovery resistance: The local energy dissipation in a specimen just below the indenter is a usual trend for the indentation induced measurement. The capacity of this energy dissipation was measured by evaluating the Recovery resistance ($R_s$) of any material

\[
R_s = 2.263\left(\frac{E_r^2}{H}\right)
\]

by equation (7). However, the localized plastic flow of a material (discussed in the section 3.3.3) is closely related with this parameter and gives the necessary evidence for the observable fact. Furthermore, Bao et al. [26] reported that the increase in recovery resistance
actually signify the rise of localized plastic flow in a specimen. Here, the calculated $R_s$ values of the lead silicate glass and the composite were found to be $1.44 \times 10^{12}$ and $1.59 \times 10^{12}$ respectively. The increment of this parameter eventually established the enhanced localized plastic flow in the composite material compared to the base glass.

3.4 Conclusions: The promising aspect of an entity as reinforcing filler depend not only the character of the material but also the technique by which it can be incorporated in a host matrix. In many cases reinforcement methods were failed to improve the mechanical properties of the fabricated composite. In fact, CNT incorporated different composite materials were not the exceptions in this abovementioned framework. Considering the CNT-glass composites one can conclude that other methods like sol-gel, hot press etc. were capable to increase the hardness with the reduced toughness of the composite or vice-versa. On the other hand the melt-quench technique has succeeded to enhance both the hardness and the toughness of the composite material than that of the base glass. The cushion-like character of the entangled SWCNT bundles was the main responsible factor for the hardness improvement whereas the significant increment in the fracture toughness value aroused due to the enhanced localized plastic flow in the composite. Moreover other mechanical parameters, i.e, Young’s modulus, Reduced Young’s modulus and the Recovery resistance were increased in the SWCNT-lead silicate glass composite than the base glass. From this point of view it can be stated that the melt-quench route was established as an efficient technique for the overall improvement in the mechanical and the structural aspect of the material. Thus one can conclude that SWCNT acts as a potential reinforcing agent in this composite such that it can be considered as a prospective material for air crafts and different structural applications.
3.5 References:


