Investigation on elastic properties and radiation shielding of Lead-recycled Cathode Ray Tube glass system

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Original Article

Investigation on elastic properties and radiation shielding of Lead-recycled Cathode Ray Tube glass system

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Abstract

The elastic and radiation shielding properties of lead-recycled CRT glass were investigated in order to study the possibility to reduce the use of toxic lead oxide glass by partially replacing with CRT glass waste. The elastic properties of lead-recycled glass were studied by using pulse-echo ultrasonic technique and, it was found that the elastic properties varied with CRT content in the glass. This indicates the existence of some modifying cations in CRT. The radiation shielding properties of the glass were also studied by means of calculated mass attenuation coefficient ($\mu_m$), mean free path (mfp) and half value layer (HVL) using WinXCom program. The addition of CRT was found to deteriorate the radiation shielding properties of lead glass. However, lead-recycled CRT glass still exhibited a better radiation shielding properties than the standard shielding concrete (barite concrete). Therefore, lead-recycled CRT glass can be a potential candidate for radiation shielding applications.
**1. Introduction**

With the significant advances in the development of display technology of television, Cathode Ray Tube (CRT) monitor was displaced by Liquid Crystal Display (LCD), Plasma Display Panel (PDP) and display made of Organic Light Emitting Diode (OLED) (Poon, 2008; Andreola, Barbieri, Corradi, & Lancellotti, 2007). These new television displays can realize the higher definition image, lower energy consumption and reduced eyestrain issue. Therefore, instead of repairing or reusing, many CRT monitors have been discarded as Electronic-Waste (E-Waste). This E-Waste includes a term for electronic products that have become unwanted, out-of-date and non-working. The CRT monitor is usually made up of 4 types of glass components (panel, cone, and neck and frit junction) and these CRT glass components can be accounted for 50% to 85% of the total weight of CRT monitor (Jaeger, 1975; Zughbi, Kharita, & Shehada, 2017; Xing et al., 2018). For electronic radiation protection purposes, some heavy metals (e.g. lead, barium and strontium) were added during manufacturing process of these CRT glass components. Cone and neck glasses at least contain high amount of lead (Pb) and panel glass contains barium (Ba) and strontium (Sr) (Andreola, Barbieri, Corradi & Lancellotti, 2007; Hui & Sun, 2011). Because of high toxicity of these heavy metals, especially lead (Pb), waste management of discarded CRT glass has become a global environment problem (Hui & Sun, 2011; Socolof, Overly & Geibig, 2005; Andreola, Barbieri, Corradi & Lancellotti, 2007). In Thailand, disposal of CRT waste is rising sharply. It was predicted that in 2010 about 1.5 million televisions and 1.5 million...
computers were discarded improperly by burying them (Sua-iam & Makul, 2013; Rahad, 2015). Toxic metal can leach into the ground and effect environment and human health. In order to reduce the disposal of CRT glass, many researchers have tried to reuse and recycle them such as the use of crushed discarded-CRT glass in many types of concrete such as barite concrete (Ling & Poon, 2012; Zhao, Poon & Ling, 2013; Ling & Poon, 2014). Some researchers has tried to use this concrete as radiation shielding material however there are many unavoidable disadvantages: (1) Generally, after prolonged exposure to nuclear radiation, formation of crack occurs in concrete due to arising of tensile stress from volume change when undergoes shrinkage, settlement, thermal stress, hydration heat, weather and load, (2) After absorption of radiation, concrete becomes hot and loss of water can occurs, this lead to an uncertainty in its shielding properties, and (3) This shielding concrete is opaque so it is impossible to see inside the shielding area (Kaundal, Kuar, Singh & Singh, 2010; Singh, Kaur & Kuandal, 2014). From the limitations of concrete a, glass researchers has utilized the transparent metal oxide glass as radiation shielding materials. It was found that one of the excellent radiation shielding glass is lead oxide glass, which can be used as X-ray observation equipment (Kaundal, 2016). However, lead oxide is toxic to environment.

This research is aimed to reduce the use of lead oxide by partially replacing with CRT glass waste. Firstly, chemical composition of the glass components of CRT monitor was analyzed and then it was mixed with lead oxide (Pb$_3$O$_4$) during manufacturing process. After that elastic properties of the lead-recycled CRT glass were investigated by using pulse-echo ultrasonic technique. Moreover, their radiation shielding properties was evaluated by WinXcom program and compared with that of the standard nuclear radiation shielding concrete (barite concrete).
2. Materials and methods

2.1 CRT preparation and characterization

The cathode ray tube (CRT) glass for this research was acquired from the display components of desktop computer monitor. The CRT glass was crushed into a fine powder using a mortar. The elemental analysis of CRT glass was conducted by using Energy Dispersive X-ray Spectroscopy (EDS) technique and shown in Table 1. It reveals the significant amounts of oxygen (O) and silicon (Si) with small amounts of barium (Ba), sodium (Na), Potassium (K), lead (Pb), calcium (Ca), aluminum (Al), and magnesium (Mg).

2.2 Lead-recycled CRT glass preparation

The glass system of (x)CRT - (100-x)PbO glass, where x = 0, 10, 20, 30 and 40 mol%, were prepared by the conventional melt quenching method. The mixture of crushed CRT glass and Pb₃O₄ were melted in ceramic crucibles at around 1,250 °C. After 2 h of melting process, the molten glass was quickly poured into warmed stainless steel molds and annealed at 540 °C for 2 h, followed by slow cooling to room temperature. The samples of lead-recycled CRT glass were then cut, grinded and polished to obtain flat, parallel end face for ultrasonic velocity measurement with straight and angle beam probes.

2.3 Density and molar volume

Archimedes’ principle was applied to determine density at room temperature of the lead-recycled CRT glass by using n-hexane as immersion liquid. The density was calculated by applying the following relation (Gaafar & Marzonk, 2007)
\[
\rho = \rho_{im} \left( \frac{W_{air}}{W_{air} - W_{im}} \right)
\]  

(1) 

where \( \rho_{im} \) is the density of immersion liquid at room temperature. \( W_{air} \) and \( W_{im} \) are the weight of lead-recycled CRT glass in air and in immersion liquid, respectively.

The molar volume \( (V_m) \) of the lead-recycled CRT glass can be determined by the following relation (Laopaiboon, Bootjomchai, Chanphet & Laopaiboon, 2011).

\[
V_m = \frac{M}{\rho}
\]  

(2) 

where \( M \) is the molecular weight of the lead-recycled CRT glass. All measurements were repeated three times for accuracy.

### 2.4 Ultrasound velocity measurement and elastic properties analysis

The velocities of ultrasonic wave in lead-recycled CRT glass were evaluated using pulse-echo technique at 4 MHz frequency with ULTRAGEL II (MAGNAFLUX) as a couplant. Elapsed time between the transmitter and the receiver of the pulse were measured and then used to calculate the ultrasonic velocities by the following relation (El-Mallawany & El-Khoshkhany, Afifi, 2006; Marzouk & Gaafar, 2007).

\[
v = \frac{2x}{\Delta t}
\]  

(3) 

where \( x \) is thickness (cm) of the sample and \( \Delta t \) is the time interval (s\(^{-1}\)).

Longitudinal and shear ultrasonic velocities \((v_l \text{ and } v_s, \text{ respectively})\) and density \((\rho)\) of the glass samples were then applied to calculate the elastic moduli, Poisson’s ratio and micro-hardness by using the following relation (Afifi & Marzonk, 2003).

**Longitudinal modulus:** \( L = \rho v_l^2 \)  

(4) 

**Shear modulus:** \( G = \rho v_s^2 \)  

(5) 

**Bulk modulus:** \( K = L - \left( \frac{4}{3} \right)G \)  

(6)
Young’s modulus: \[ E = 2(1 + \sigma)G \] (7)

Poisson’s ratio: \[ \sigma = \frac{L - 2G}{2(L - G)} \] (8)

Micro-hardness \[ H = \frac{(1 - 2\sigma)E}{6(1 + \sigma)} \] (9)

2.5 Structural Analysis by FTIR techniques

Structure of the lead-recycled CRT glass was also analyzed by using Fourier transform infrared spectroscopy. The standard KBr pellet-preparing methods were applied. Then FTIR transmission spectra have been recorded in the wavenumber range of 1200-400 cm\(^{-1}\).

2.6 Shielding properties analysis

The radiation shielding properties of lead-recycled CRT glass was evaluated by means of mass attenuation coefficient \((\mu_m)\), mean free path \((mfp)\) and half value layer \((HVL)\). The mass attenuation coefficient for selected radiation energy of 662, 1173, and 1332 keV (which represent the radiation for the radioisotope source of \(^{137}\)Cs and \(^{60}\)Co, respectively) was evaluated by using WinXCom program developed by national institute of standard and technology (NIST). Based on mixture rule, the \(\mu_m\) for mixture of elements can be written as

\[ \mu_m = \sum w_i (\mu/\rho)_i \] (10)

where \(w_i\) and \((\mu/\rho)_i\) are weight fractions and mass attenuation coefficients of the constituent elements, respectively (Gerward, Guilbert, Jensen & Leyring, 2001, 2004).

Then the \(\mu_m\) of the lead-recycled CRT glass was used to calculate its \(mfp\) and \(HVL\) by using the relation (Bootjomchai, Laopaiboon, Yenchai & Laopaiboon, 2012):

\[ mfp = \frac{1}{\mu_m} \] (11)

\[ HVL = 0.693/\mu_m \] (12)
The calculated mfp and HVL were then compared to that of standard shielding concrete (barite concrete).

3. Results and Discussion

3.1 Density and molar volume

Variation of experimental values of density and molar volume with CRT content is shown in Figure 1. It can be seen that with increasing the CRT content, density of lead-recycled glass decreases. The decrease in density can be explained by the fact that atomic mass of Si (28.08 g/mol), Na (22.98 g/mol), Mg (24.30 g/mol), Al (26.98 g/mol), K (39.09 g/mol), Ca (40.07 g/mol) and Ba (137.32 g/mol) of CRT are all lower than 207.2 g/mol of Pb. Figure 1 also shows a linear decrease of molar volume of the glass with increasing CRT concentration. Generally, a reduction in molar volume indicates a decrease in atomic spacing between atoms (Singh & Singh, 2013). This can be applied to explain the decrease of molar volume of the lead glass with addition of CRT since ionic radius of Si$^{4+}$ (0.54Å), which is the main cation from CRT, is much smaller than 1.19Å of Pb$^{4+}$.

3.2 Ultrasonic velocity

In general, the change in ultrasonic velocities relates to a change in number of non-bridging oxygen (NBO); in other word, it relates to a change in connectivity of the glass network. Therefore, the ultrasonic velocities reveal the degree of structural change in the glass (Bootjomchai, Laopaiboon, Yenchai & Laopaiboon, 2012). Figure 2 shows longitudinal and shear ultrasonic velocities ($v_l$ and $v_s$) in lead-recycled CRT glass with different CRT content. Generally, addition of CRT leads to a change in both ultrasonic velocities, indicating a change in number of NBO in the glass network. With small addition of only 10 mol% of CRT, both velocities decrease, possibly imply an enter of
cation from CRT to the lead glass network by breaking some bonding of Pb-O-Pb. However, a further increase in CRT content to 20 and 30 mol% results in an increase of the velocities, showing a creation of a glass network with network bonding of such as O-Si-O. Both velocities decrease again when content of CRT increase further up to 40%. This reveals a breakdown of the glass network again when concentration of CRT is higher. Therefore, results from ultrasonic velocities measurement exhibits a change in glass network by insertion of cationd (e.g., Si$^{4+}$ and Mg$^{2+}$) from CRT.

3.3 Elastic properties

The elastic properties of lead-recycled CRT glass were studied by means of longitudinal modulus (L), Shear modulus (G), Bulk modulus (K), Young’s modulus (E), Poisson’s ratio (σ) and micro hardness (H). The formulas used for calculation are given in equations (4) - (9). From the formulas, it can be expected that the factors that influence the ultrasonic velocities in the glass also affect its elastic moduli. It was found from Figure 3(a), (b) and (c) that the values of longitudinal, shear and Young’s moduli were found to be decreased when addition of CRT is only 10 mol%. This can be attributed to the breakdown of glass structure. However, when the addition of CRT increase to 20 mol%, these moduli rise up. The increase in these moduli may be ascribed to an effect of stronger field strength of silicon cation (e.g. Si$^{4+}$) from CRT (Du, 2009). This implies the present of O-Si-O bonds in the glass structure. Then a further increase of CRT up to 30 mol% results in a reduction in these moduli, which disagrees with the result from ultrasonic velocities. Therefore, this decrease in the moduli with an increase in ultrasonic velocities can be attributed to the competition between decrease of density and rising in field strength of silicon cation. When CRT content increase to 40%, a further decrease of the moduli was observed, indicting a further reduction in the moduli.
due to the breakdown of glass structure again. The bulk modulus, which describes the resistance to deformation of material under pressure on all surfaces, in Figure 3(d) shows slightly different trend. With the small addition of 10 mol% of CRT, the bulk modulus decreases. This may imply that the oxygen bonds in the lead glass structure are destroyed by cation from CRT, creating NBOs. This results in the formation of open structure, characterized by many open space (Marzouk, 2010). With further addition of CRT from 10 to 30 mol%, the increase in bulk modulus is observed, indicating the more compact structure. The more compact structure can be attributed to a reduction of NBOs by formation of oxygen bonding with silicon cations as well as a filling up of open space by silicon cation. However, the addition of more CRT to 40 mol% sharply reduces the bulk modulus again, possibly implying the breakdown of glass structure again (Sidek, Bahari, Halimah & Yunus, 2012).

Poisson's ratio of the lead-recycled CRT glass also changes with content of CRT as shown in Figure 4 (a). This observation supports that there is a change in cross-link density with the addition of CRT, as it is well known that the change in cross-link density results in the alteration of Poisson’s ratio. Generally, a Poisson's ratio of the glass with high cross-link density is in the range 0.1 to 0.2, while that with low cross-link density exhibit a Poisson's ratio between 0.3 and 0.5 (Rajendran, Palanivelu, Chauduri & Goswami, 2003). In this present study, Poisson's ratio is lower than 0.3, suggesting a high cross-link density of our lead-recycled CRT glass. The rise of Poisson's ratio when addition of CRT is only 10 mol% indicates the reduction of cross-link density due to breakdown of the glass network. When addition of CRT increase to 20 mol%, Poisson’s ratio decrease, implying an increase of cross-link density due to an insertion of cation in to the glass network with lower atomic packing density. However, when further increase CRT
content to 30 mol%, Poison’s ratio surprisingly and largely increases again, implying a higher atomic packing density. This exhibit stronger influence of a filling up of free space by silicon cation than formation of O-Si-O in the glass network. Therefore, when CRT concentration increase to 40 mol%, Poison’s ratio drops down again, implying the increase of free space due to an influential breakdown of glass structure (Rouzel et al., 2008). This means when most free space is filled; more addition of silicon cations leads to a breakdown glass structure again.

Micro-hardness describes the stress required to eliminate the free volume of the glass. It can be seen from Figure 4 (b) that micro-hardness change with concentration of CRT. The addition of 10 mol% CRT results in a decrease in micro-hardness of the glass due to a breakdown of the glass structure. When increase the addition of CRT to 20 mol%, maximum micro-hardness is reached. This indicate a strengthening of the lead-recycled CRT glass due to an introduction of stronger ionic bond (e.g. O-Si-O) in the lead-glass structure. However, with further addition of more CRT, micro-hardness of the lead-recycled glass decrease, which can be contributed to an influence of large decrease in density due to the substitution of Pb$^{4+}$ by Si$^{4+}$.

Therefore, all result from ultrasonic measurement suggests that the addition of CRT leads to a change in dimensionality of the glass structure and also a change in the cross-link density (Rajendran, Palanivelu, Chauduri & Goswami, 2003).

3.4 Structural analysis by FTIR spectroscopy

The FTIR transmission spectra can be divided in to 2 active regions: (Region 1) 400-600 cm$^{-1}$ is related to bending vibration of Si-O-Si of SiO$_4$ (440-460 cm$^{-1}$) and stretching vibration of Pb-O-Pb of PbO$_4$ (498-507 cm$^{-1}$) and (Region 2) 800-1200 cm$^{-1}$ can be attributed the presence of a Si-O-[NB] asymmetrical vibration mode (850-1200 cm$^{-1}$) and
Pb-O asymmetrical bending vibration mode (1090 cm⁻¹) (Ramadevudu et al., 2012; MacDonals, Schardt, Masiello & Simmons, 2000; Rada, Dehelean & Culea, 2011; Rao et al., 2012; Bosca, Pop, Pascuta & Culea, 2009).

It can be seen form Figure 5 that when the addition of CRT content is 10%, the intensity of the obvious peaks in region (1) decrease but the intensity of the broaden peaks in region (2) increase. This imply the formation of NBOs by breaking down the Pb-O-Pb bonding and formation of asymmetric Pb-O bond. However, with a further addition of CRT content to 20%, Peaks intensity in region (1) has grown back and the disappearance of IR peaks in region (2) was observed. This may relate to a reduction of NBOs by the formation of O-Si-O in the glass network. However, with further increase of CRT content to 30%, no significant difference was detected, implying insignificant formation of more O-Si-O bonds. Therefore, the excess cations from CRT mainly fills up the free space in the glass structure. When increase the addition of CRT to 40%, the decrease of IR peak in region (1) with a presence of indistinct peaks in region (2) suggest the formation of few NBOs again. This observation is also consistent with the variation in ultrasonic velocities.

3.5 Radiation shielding properties

Mass attenuation coefficient (μm), mean free path (mfp) and half value layer (HVL) are important parameters to estimate radiation shielding properties of the glass systems (Kaur, Singh & Anand, 2015). The values of μm for radiation energies of 662, 1173 and 1332 keV were calculated using WinXCom program. Figure 6 exhibits the variation of μm as function of CRT content for all radiation energies. It has been found that the μm values slightly decrease with the increment of CRT content. This can be explained by a decrease in densities of lead-recycled CRT glass. Therefore, for all radiation energies, the
addition of CRT to lead-glass only results in a small reduction in its shielding properties (Kaur, Singh & Pandey, 2014).

Figure 7(a) exhibits a variation of mean free path ($mfp$), which is the reciprocal of measured linear attenuation coefficient, of lead-recycled CRT glass as function of CRT content. It can be observed that the calculated $mfp$ slightly increases with increasing CRT content. This indicates that with increasing CRT content, the longer distance to suppress and attenuate the incident radiation is required. Therefore, the more the concentration of CRT, the poorer the shielding properties of the lead recycled CRT glass. Nevertheless, when compare $mfp$ value of lead-recycled CRT glass with a standard shielding concrete like barite concrete, it is found that $mfp$ value of lead-recycled glass with all CRT content is lower than that of barite concrete, indicating a better shielding properties of the lead-recycled glass than barite concrete for all radiation energies.

Half value layer ($HVL$), which is the thickness of material where the intensity of radiation passing through it is decreased by 50%, of lead-recycled CRT glass as function of CRT content is shown in Figure 7(b). It is observed to slightly increase with increasing CRT content for all radiation energy. This increase in $HVL$ indicates a reduction in the shielding properties of the lead-recycled CRT glass in a term of thickness requirement. However, it is also found that the $HVL$ value of lead-recycled CRT glass are all lower than that of barite concrete, indicating a better shielding properties of lead-recycled CRT glass for all radiation energy. Therefore, by means of $mfp$ and $HVL$, the lead-recycled CRT glass has a potential to be a better radiation shielding material in comparison to barite concrete.

4. Conclusions
Lead-recycled Cathode Ray Tube (CRT) glass was prepared from the mixture of crushed CRT and Pb$_3$O$_4$ using conventional melt quenching methods. The properties of lead-recycled CRT glass were studied as a function of CRT content. It was found that density and molar volume of lead-recycled CRT glass decrease with increasing CRT content, indicating the partial substitution of lead oxide network by cation from CRT such as Si$^{4+}$. The elastic properties of the lead-recycled CRT glass were investigated by using pulse-echo ultrasonic technique. The variation of both longitudinal and shear ultrasonic velocities as function of CRT content was also observed. This exhibits that addition of cations in CRT leads to a change in network structure of the glass. The network-modifying cation breakdowns the Pb-O-Pb bonding, creating NBOs, and also form O-Si-O network bonding. Thus, the elastic moduli of lead-recycled CRT glass were also found to vary with CRT content. The radiation shielding properties of lead recycled glass for radiation energy of 662, 1173 and 1332 keV also were studied by means of calculated Mass attenuation coefficient ($\mu_m$), mean free path ($mfp$) and half value layer ($HVL$) using WinXCom program. It was found that the more the addition of CRT content, the poorer the shielding properties. However, when compare with standard radiation shielding concrete (barite concrete), lead-recycled CRT glass exhibited a better radiation shielding properties.

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Figure 1 Variation of density and molar volume of lead-recycled CRT glass as function of CRT content.

Figure 2 Variation of longitudinal and shear ultrasonic velocity in lead-recycled CRT glass as function of CRT content.
Figure 3 Variation of longitudinal (a), shear (b), Young’s (c) and Bulk (d) moduli of lead-recycled CRT glass as function of CRT content.

Figure 4 Variation of Poison’s ratio (a) and Micro-hardness (b) of lead-recycled CRT glass as function of CRT content.
Figure 5  FTIR spectra of lead-recycled CRT glass

Figure 6 Variation of mass attenuation coefficient of lead-recycled CRT glass as function of CRT content.
Figure 7 Variation of mean free path (a), and Half value layer (b) of lead-recycled CRT glass as function of CRT content.
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Table 1 Chemical analysis of CRT glass by EDS techniques