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Spectroscopic Interrogations and Study on the Insulating Property of Vermiculite Based Weathering Tiles

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Abstract : Vermiculite is a versatile mineral because of its thermal stability and inertness. All the five grades of vermiculites both in raw and exfoliated vermiculite forms have vast applications. The grade **V** exfoliated vermiculite is used as the weathering proof material for building constructions. It keeps interior cool in summer and reduces heat loss in winter. The FTIR-ATR spectra of pathway tiles, cement vermiculite and granite vermiculite weathering tiles samples have been recorded in the mid - infrared region of 4000-450 cm^{-1}. In general, vibrational spectroscopy detections can qualitatively and quantitatively distinguish the spectral assignment of specific bands between corresponding bonds and functional groups, as also the observation of spectral profiles can be used to define and differentiate the pathway tiles, cement and granite vermiculite tile. The present work is aimed to make an investigation with reference to the insulating property of the vermiculite tiles. The diffusion reflectance spectroscopy technique confirms that with increase in wavelength, the band gap energy decreases. Further, UV-Vis measurements prove the reduction of optical band due to increase of structural disorder of cement vermiculite tile, granite vermiculite tile and pathway tile. The dielectric measurements were carried out to analyze the insulating property of cement and granite vermiculite tiles. It is observed that dielectric constant and dielectric loss of vermiculite decrease with increase in frequency. However cement vermiculite tile to granite vermiculite tile it is noted that there is an increase in the dielectric strength of the material, as it possess low dielectric constant as well as dielectric loss.
Keywords : Cement vermiculite tiles, Granite vermiculite tile, Pathway tile, Composites, FTIR-ATR, UV-Visible, dielectric measurements.

Introduction

Vermiculite is a geological name given to the group of Hydrated Laminar Minerals Vermiculite is a natural mineral that expands with the application of heat. Vermiculite is a safe inert material and light in colour. The expansion process is known as exfoliation and it is routinely accomplished in purpose-designed commercial furnaces. Its chemical formula is $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O$. Vermiculite is formed by weathering or hydrothermal alteration of biotite or phlogopite. Countries such as Australia, Brazil, China, Kenya, USA, Zimbabwe, Uganda and India have commercial vermiculite mines. The largest vermiculite mine (by production) in the world is Palobora which is in South Africa [(2)]. In India, vermiculite is available at Thirupathur, Tamilnadu, India.

Of the five grades of exfoliated vermiculite, grade is used as the weathering proof material in industries. A mixer of cement and grade **V** exfoliated vermiculite as well as granite and grade **V** exfoliated vermiculite are used as roof tiles materials when there are mixed in the ratio of 2:1 respectively. Such roof tiles are of light in weight, which can be used as a slope to drain, not only shed water but can reduce the steel structure design of providing a smooth insulating roof substrate for the roof membrane [(8)]. They provide thermal insulation to computer rooms; cold storages etc. as the product arrest the heat dissipation [(3)]. The pathway tiles are used in the garden places. Vermiculite is a fire proof material and used as a carrier for agricultural and industrial applications [(6)]. Consequently the mineral has become a pre-dominant area of research having a key role in the economic growth of a nation.

Cement vermiculite tile:

Cement vermiculite tile is obtained by mixing cement and grade **V** exfoliated vermiculite in the ratio of 2:1 respectively. The strength of the cement vermiculite tile is determined after 7 days curing [(7,3)]. The polymer layer which are formed on the cement particles surface as a result of water inside the surface contribute towards hydration of cement vermiculite tile. Vermiculite cement tile posses low water absorption, better strength, and high insulation.

Granite vermiculite tile:

The old age granite rocks of Tamilnadu have become popular in international market for their peculiar characteristics such as high specific gravity, strength and polishing capacity [(9)]. The granite mixed with exfoliated vermiculite in the ratio of 2:1 respectively. Based on the results, it can be concluded that vermiculite granite tiles exhibit high strength, high refractoriness, low thermal conductivity and adequate chemical inertness. They also exhibit low insulation compared to the conventional cement tile which are especially used for insulation purpose. The granite vermiculite tile is well suited to construction industries



Cement vermiculite tiles **Pathway tiles** **Granite vermiculite tiles**

Fig.1 Types of Tiles

Pathway tile:

A paver or pathway tiles is a stone tile. It is commonly used for exterior flooring. In a factory, concrete pathway tile is made by pouring a mixture of concrete and some type of coloring agent into a mold of some shape and allowing a set [(4)]. Pathway tile are obtained by the scaffolding of concrete foundation, sand and the pathway tile of the desired pattern at the top. The figure of tiles are shown in Fig.1

Experimental and Methods:

FTIR-ATR Technique:

The vermiculite tiles were purchased from Tamilnadu minerals, Chennai, India. FTIR-ATR technique is well recognized for qualitative analysis in the case of solids. This method is suitable in examining the quality of cement mixed grade **V** vermiculite tile, granite mixed grade **V** exfoliated vermiculite tile and pathway tile. FTIR-ATR spectra of vermiculite were analyzed by using FTIR spectrometer with diamond ATR accessory. By using Spectrum Two Perkin-Elmer FTIR spectrophotometer using 16 scans and instrument resolution of 4 cm^{-1}. The total measurement time was approximately 32 second. The Fourier transform infrared spectra of vermiculite (Cement vermiculite tile, granite vermiculite tile and pathway tile) were recorded at room temperature. The measurements of cement vermiculite tile, granite vermiculite tile and pathway tile were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), St. Peter's Institute of Higher Education and Research, St. Peter's University (SPU), Avadi, Chennai-54. The FTIR-ATR spectra of cement vermiculite tile, granite vermiculite tile, pathway tile samples have been recorded in the Mid-infrared region of 4000-450 cm^{-1} as shown in the Fig. 2.

UV-Vis Technique:

The acquired diffuse reflectance spectrum is converted to Kubelka-Munk function. The Kubelka–Munk model allows calculation of reflectance from a layer that both scatters and absorbs light. It is a 'two-flux' model, which means that only diffuse light is considered. The diffuse reflectance of the samples is measured using a spectrophotometer fitted with a diffuse reflectance attachment. Vermiculite samples indicate that, the DRS technique is not as sensitive as the UV-Vis absorption of the sample which is recorded in the range of 200-800 nm using Perkin-Elmer spectrophotometer. In UV-Vis absorption no solvent is used. The spectral measurements were carried out at Sophisticated Analysis Instrumentation Facility, St. Peter's University at Chennai in India. The spectra of cement vermiculite tile, granite vermiculite tile and pathway tile are shown in Fig. 3

Dielectric Analysis:

The dielectric measurement was carried out at Department of Physics, Loyola College, at Chennai. The dielectric studies of vermiculite were analyzed using HIOKI model 3532-50 LCR HITESTER with a conventional two terminal sample holder. The dielectric studies were carried out for varying frequencies from 50Hz to 5MHz at room temperature are shown in Fig 4.

Results and Discussion

FTIR-ATR Analysis:

A vibrational band assignment is carried out with the idea of group frequencies of the different composition which are present in the sample. The insulation properties of vermiculite have been studied by observing the intensity and shape of the specific modes of vibrations. The spectra consist of characteristic bands of silicate, aluminum, alkali, iron, and water. In the infrared region, characteristic bands of the cement vermiculite tile, granite vermiculite tile and pathway tile samples were found: Si-O stretching bands are found near 970-995 cm^{-1} and above 712 cm^{-1} Al-O stretching band are obtained[(1)]. The bands above 3391 cm^{-1}, 3234 cm^{-1} and 3649 cm^{-1} are attributed to O-H stretching vibrations of hydroxide in the inner layer sheets[(5)].

Infrared spectrum of the examined sample showed band in the wave number range 1647 $cm^{-1}$and 1638 cm^{-1} are due to H_2O bending. Fundamental vibrations of CO_3^{2-} in calcite arise at 713 cm^{-1}. The mixed combination band of Si-O of quartz is at 672 cm^{-1} and 872 cm^{-1} is attributed to the Fe_2O_3 band [(9)]. The recorded spectra of vermiculites in cement vermiculite tile, granite vermiculite tile and pathway tile are shown in Fig.2 respectively. The SiO_2 stretching band for pathway tile are observed the wave at 962 cm^{-1}, the cement tile is at 992 cm^{-1}, and the granite vermiculite tile is at 988 cm^{-1} respectively [(10)]. It can be confirmed that the presence of silica is highly in cement vermiculite tile which are shown in Table 1. It can be confirmed that the pathway tile show less mechanical and thermal stability because of the silica which is observed at 967 cm^{-1} compared to the other cement and granite vermiculite tiles [(11)]. The spectral bands of the hydrated water molecules that are recorded in pathway tile reveal the existence of water molecules as is observed the OH group at 3649 cm^{-1} which is high compared to the other vermiculite tiles. The high absorbance of OH group in pathway tile implies that the water molecules are suppressed due to the mixing of cement and granite in the case of cement vermiculite tile and granite vermiculite tile. The OH band for cement vermiculite tile is observed at 3391 cm^{-1} and granite vermiculite tile is observed at 3234 cm^{-1}.

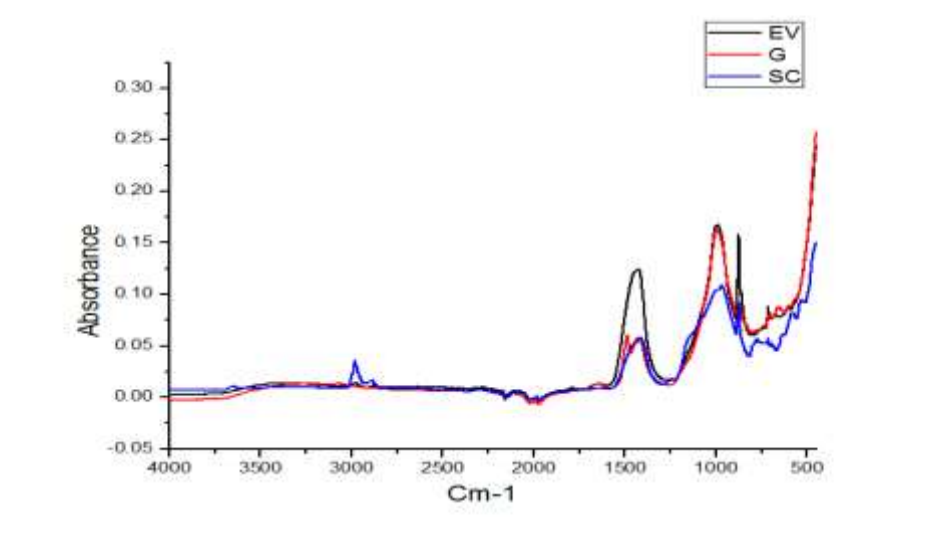

Fig.2 FTIR-ATR overlaid spectra of cement vermiculite tile, granite vermiculite tile and pathway tile

Table 1 FTIR-ATR Spectral Analysis of Cement Vermiculite Tile, Granite Vermiculite Tile and Pathway Tile

Cement vermiculite tile	Granite vermiculite tile	Pathway tile	Assignment
3391	3234	3649	OH Stretching
1638	1646	1647	H_2O bending
1425	1486	1411	Alkali band
992	988	967	SiO_2 band
874	872	874	Fe_2O_3 band
712	-	712	In plane bending of calcite orAl-O band
672	-	-	SiO_2 of quartz
533	-	-	SiO_2 asymmentric bending

By adding cement to the vermiculite tile an increase in thermal stability and mechanical strength is observed by the presence of silica at 992 cm^{-1}. The comparison of overlaid spectra is shown in Fig.2. Internal ratio parameters are calculated with the reference to stretching vibrations of SiO_2 at 982 cm^{-1} intensity band observed in the FTIR spectra for cement vermiculite tile, granite vermiculite tile, and pathway tile are summarized in Table 2.

Table 2 Internal Standards Ratio parameters values of Cement, Granite vermiculite tiles and Pathway tile

Specific modes of vibration	Description	A_{982}/A_X		
		Cement vermiculite tile	Granite vermiculite tile	Pathway tile
3424	OH Stretching	1.015	1.014	1.001
1643	H_2O bending	1.013	1.012	1.011
1440	Alkali band	1.009	1.004	1.003
982	SiO_2 band	1.000	1.000	1.000
873	Fe_2O_3 band	1.009	1.006	1.002
712	Al-O band	1.007	-	1.004

UV-Vis Analysis:

The UV–Vis spectral analysis of vermiculite has been calculated by band gap energy method UV–Vis spectrum of cement vermiculite tile, granite vermiculite tile and pathway tile are shown in Fig.3. The Kubelka-Munk model is the basis for measurements of the band gap of thick powder samples. Band gap indicates that the difference in energy between the bottom of the valence band which are filled with electrons and the top of the conduction band which are devoid of electrons [12,16]. The band gap is related to the electric conductivity of the materials. The band gap values are shown using the typical eV unit, but these values are also presented in nm in parentheses for comparison with the actual data of the diffuse reflectance spectra [14]. It is clear that the values presented in nm correspond well with the absorption edge wavelengths of the diffuse reflectance spectra. This note demonstrates how the band gap of a material can be determined from the UV absorption spectrum. The band gap energy of cement vermiculite tile is better compared to granite vermiculite tile and pathway tile are shown in Fig.3 and the results are shown in Table 3.

To calculate the Band gap energy:

Using the formula of $E = h*c/ \lambda$
E= Energy in joules
h=Planks constant=$6.626x\ 10^{-34}$ Joules/sec
c=Speed of light=$2.99x\ 10^{8}$ meter/sec
λ =Wavelength

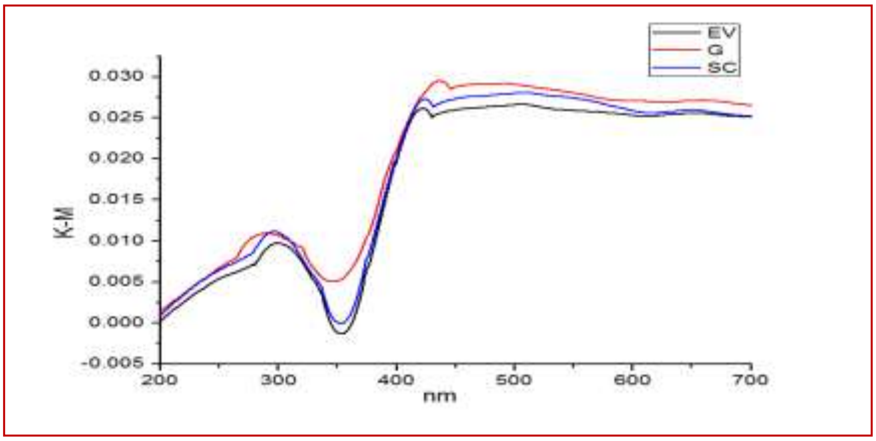

Fig.3 Overlaid UV-Vis Spectra of Cement vermiculite tile, Granite vermiculite tile and Pathway tile

Table 3 Band Gap Energy Values of Cement Vermiculite Tile, Granite Vermiculite Tile and Pathway Tile

Tiles	**Cut – off wavelength nm**	**Band gap energy**
Cement vermiculite tile	343	3.610
Granite vermiculite tile	350	3.537
Pathway tile	356	3.478

The band gap energy is increased in cement vermiculite tile which is shown in Table 3 as a comparison with the granite vermiculite tile and pathway tile. It can be shown that the increase of structural disorder with ion influence leads to reduction of the optical band.

Dielectric studies:

The frequency dependence on dielectric constant of the cement vermiculite tile and granite vermiculite tile is evaluated between 50Hz and 5MHz [15]. The materials are analyzed at room temperature. From the dielectric study, it can be concluded that both dielectric constant and dielectric loss of the sample decreases with increase in frequency and attain a constant value beyond 1000 Hz [13,17]. The results show that increased insulating property of cement vermiculite tile is shown in Fig.3a. Moreover decreasing trend is noticed in the value of dielectric constant (ε_r) for cement vermiculite tile which proves that the cement vermiculite tile is a better insulator than the granite vermiculite tile the Figures are shown in Fig.4.

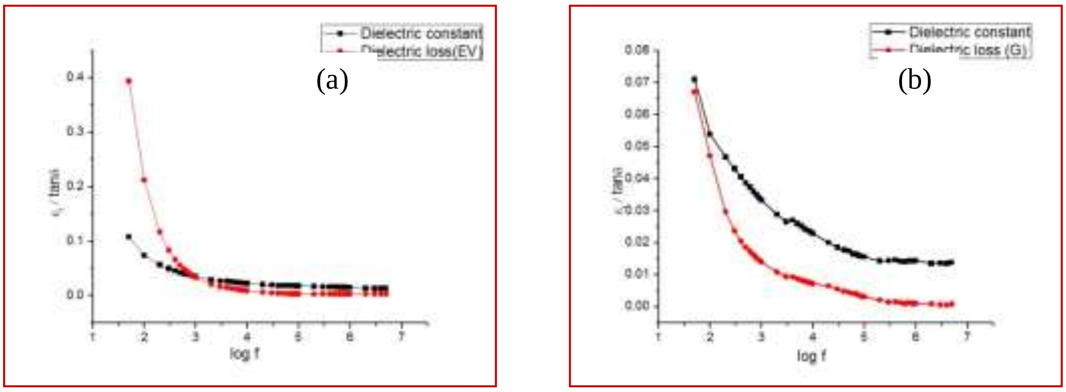

Fig.3 Dielectric studies on (a) Cement vermiculite tile and (b) Granite vermiculite tile

Conclusions

The FTIR-ATR measurement is used to analyze the samples of cement vermiculite tile, granite vermiculite tile and pathway tile. It is found that increase of vermiculite content decreases compressive strength and increases water absorption of the resulting vermiculite tile. The FTIR-ATR technique is used to identify the characteristic bands of Silicate, aluminium, iron, alkali and water present in the mineral, and a spectral analysis is also carried by FTIR-ATR. It is observed that the cement mixed vermiculite is more stable and has high mechanical strength than the other two tiles, because of the presence of silica. UV-Vis absorption results concluded that the band gap energy decreases with increase in wavelength in the sample of pathway tile, cement and granite vermiculite tile. The UV-Vis measurements made on the sample of pathway tile, cement vermiculite tile, granite vermiculite tile have proven that the increase of structural disorder with ion influence leads to reduction of the optical band. The spectroscopic instrumentation techniques are used to conclude out of the three tiles, the cement vermiculite tile has higher insulation property than the granite vermiculite tile and pathway tile. Furthermore increase of temperature the relative permittivity of the vermiculite decreases, with confirms the increase of the insulating property. Hence the dielectric measurement on the sample proves that the vermiculite becomes more insulation in its cement vermiculite tile. They are in good agreement with the FTIR-ATR, UV-Vis DRS techniques and dielectric measurement results.

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