Millimeter wave spectroscopy and materials characterization of refractive liquid crystal polymer/titania composites

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Abstract

Titanium dioxide (TiO_2 or Titania) is one of the most widely used white pigments. Titania is very white and has a very high refractive index. The high refractive index and bright white color of titanium dioxide makes it an effective opacifier for pigments. Light scattering is accomplished by refraction of light as it passes through or near pigment particles (E. McNeil and R. H. French, Multiple Scattering from Rutile TiO_2 particles, *Acta Materialia*, 48(18-19), pp. 4571–4576, 2000).

This study deals with the analysis of dielectric properties of a liquid crystal polymer/Titania composite material, in order to better understand the microstructure and the effect of dispersed titanium dioxide particles on the optical properties of the composite material.

Complex permittivity, refractive index, absorption coefficient and loss tangent of the composite material have been investigated in the millimeter wave frequency range. The measurements have been performed by using two different techniques: first, free space quasi optical spectrometer equipped with high power sources of millimetre wave radiation tuneable in the 44–90 GHz frequency range and second, Dispersive Fourier Transform Spectrometer (DFTS) in the range of 100–600 GHz.

Very low level of losses of millimetre wave radiation has been observed for all samples. Frequency dependences of complex dielectric permittivity have been determined in the broad band millimetre wave range. Strong correlation between dielectric properties and dispersed Titania volume percent has been observed by using the two different techniques.
Keywords: polymer composites, reflectivity, refractive index, quasi-optics.

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1 Introduction

During the past decade, inorganic/polymer hybrid materials have been the focus of research for their excellent electrical, optical, magnetic, optoelectronic, and enhanced mechanical properties. These hybrid materials combine the advantages of the organic polymers (lightweight, flexibility, relatively high impact resistance, and reasonable processability) and inorganic materials (strong chemical resistance, high thermal stability, and high brittleness). Optical, mechanical, and thermal properties of the hybrid materials are a function of the relative volume percent of each constituent in the composite material. Recently, the development of inorganic/polymer hybrid materials with high refractive index have attracted significant interest for electronic applications.

2 Experimental details

2.1 Free space quasi optical spectrometer

Free space quasi optical spectrometer millimeter wave technique has been successfully employed for accurate transmittance spectra measurements. Extended V – band high vacuum backward wave oscillator (BWO) is applied as a source of coherent radiation continuously tunable in millimeter wave range from 44 to 90 GHz. A couple of horn antennas and a set of polyethylene lenses are used to form a Gaussian beam as well as to focus the beam into the sample. A block diagram of BWO-based free space quasi-optical millimeter wave spectrometer is shown in Figure 1.

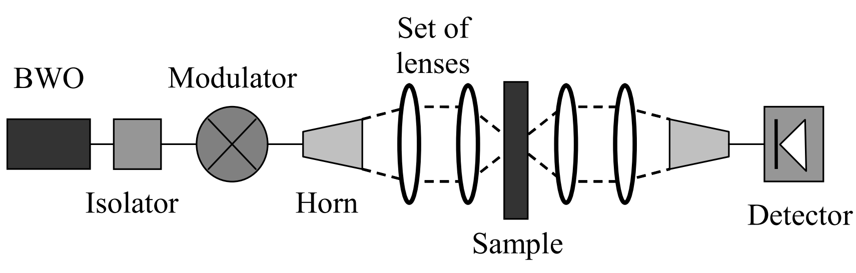

Figure 1: Block diagram of free-space quasi-optical millimeter wave spectrometer.

Details of the BWO-based free space millimeter wave spectroscopy technique, including measurements' accuracy and sources of possible errors have been discussed elsewhere [2–4].

Five slab-shaped and parallel Liquid Crystal Polymer/Titania Composite samples with different titanium dioxide concentration have been investigated. The millimeter wave measurements have been performed in a frequency sweep mode. Two consecutive frequency sweeps with and without the sample in the quasi-optical path are made and the transmittance spectra recorded. Transmittance spectral of the samples indicates very low level of losses in the millimeter waves. Additionally, real and imaginary parts of dielectric permittivity are calculated from the transmittance spectra.

After obtaining the transmittance spectra of the Liquid Crystal Polymer/Titania composite materials, optimization procedures were applied to extract the best-fit dielectric parameters of the measured samples.

2.2 Dispersive Fourier Transform Spectroscopy (DFTS)

A two-beam polarizing interferometer at the Tufts High Frequency Materials Measurement and Information Center has been utilized to perform Dispersive Fourier Transform Spectroscopy (DFTS), a popular electro-optical technique used to obtain the broadband dielectric properties of liquid, solid, powder, and gaseous samples. The interferometer's radiation source is a mercury-vapor lamp. Radiation beams from the lamp are collimated and polarized before being split in two by a wire-grid beam splitter [6, 7].

As shown in Figure 2, part of the radiation is sent to the sample chamber and the other half to a micrometer-backed moving mirror. A fixed mirror lies on the other side of the sample. After reflecting from mirrors in both chambers, the beams recombine forming an interference pattern and are consequently collected by the Indium Antimonide detector. The sample interference pattern, $V_S(x)$, varies from an empty cell reference interference pattern, $V_0(x)$, since the signal peak shifts and has smaller voltage amplitude. The difference in the interference patterns provides the two quantities, shift and thickness, required to calculate the specimens' dielectric properties [5, 6]. Extreme care has been taken to optically align the mirrors, polarizer, and beam splitter to ensure a maximum signal-to-noise ratio.

Once the two interference patterns, shift, and sample thickness are known, any multiple reflection signatures can be edited out, and a double-sided Fourier transform of the interferograms is performed to yield information in the frequency domain.

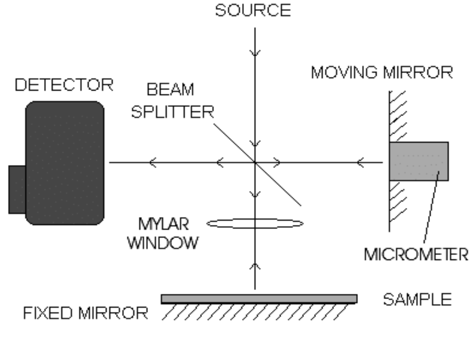

Figure 2: Diagram of the two-beam polarizing interferometer setup.

One can then proceed to calculate the five dielectric properties as follows.
The refractive index is calculated by using equation (1):

$$n(\tilde{v}) = 1 + \frac{x}{d_S} + \frac{ph\{\hat{S}_T(\tilde{v})\} - ph\{\hat{S}_O(\tilde{v})\} - ph\{\left(\hat{S}'(\tilde{v})\right)^2\}}{4\pi\ \tilde{v} d_S} \quad (1)$$

where

x	Shift
d_s	Sample thickness
$ph\{\}$	Phase of the content within the parentheses
$\tilde{v}$	Frequency
$\hat{S}_T(\tilde{v})$	Fourier transform of edited sample
$\hat{S}_O(\tilde{v})$	Fourier transform of reference sample
$S'(\tilde{v})$	Ratio of $\hat{S}_T(\tilde{v})$ and $\hat{S}_O(\tilde{v})$

Similarly, the absorption coefficient can be found by

$$\alpha(\tilde{v}) = \frac{1}{d_S}\left[\ln \frac{\hat{S}_O(\tilde{v})}{\hat{S}_T(\tilde{v})} + \ln\left(\hat{S}'(\tilde{v})\right)^2\right] \quad (2)$$

From Maxwell's equations and dielectric definitions one can calculate the loss tangent [5–7].

Complex permittivity can be calculated by using equation (3):

$$\hat{\varepsilon}(\tilde{v}) = \{\hat{n}(\tilde{v})\}^2 = \varepsilon'(\tilde{v}) - i\varepsilon''(\tilde{v}) \quad (3)$$

where

ε': real part of complex permittivity
ε'': imaginary part of complex permittivity

Refractive index can be calculated by taking the square root of the real part of permittivity and is given by equation (4).

$$\hat{n}(\tilde{v}) = \sqrt{\varepsilon'(\tilde{v})} \quad (4)$$

Finally, loss tangent can be obtained from equation (5).

$$\tan\delta = \frac{\varepsilon''(\tilde{v})}{\varepsilon'(\tilde{v})} \quad (5)$$

3 Results and discussions

Refractive index of the composite materials measured with quasi optical techniques shows that as the volume percent of the TiO_2 particles increases above 21%, the refractive index decreases at both the low and high frequencies as shown in Figure 3.

Absorption coefficient measured for all the samples, as shown in Figure 4, illustrate that at the 47 GHz frequency there is not much change in absorption coefficient (~ 0.090 nep/cm) above 22 volume percent of Titania.

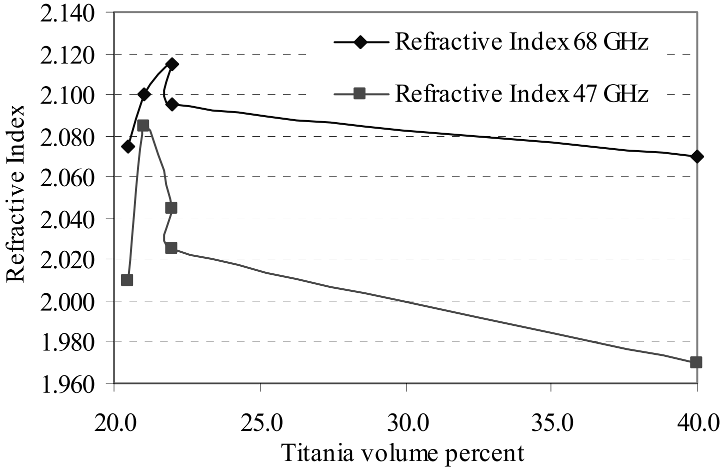

Figure 3: Refractive Index as a function of Titania volume percent at 47 and 68 GHz frequency.

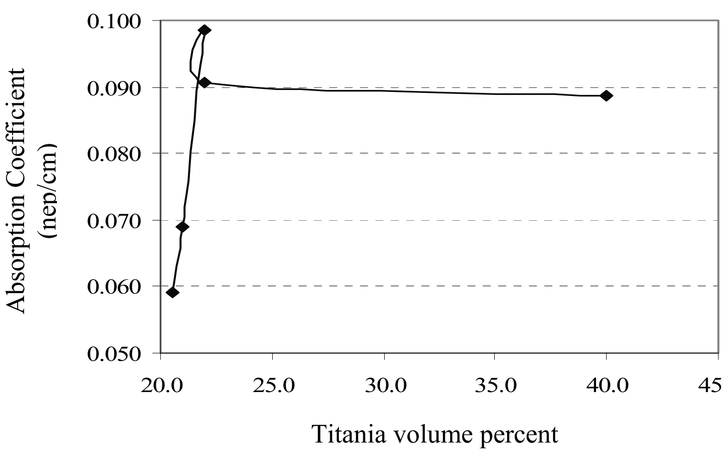

Figure 4: Absorption coefficient as a function of Titania volume percent at 47 GHz frequency.

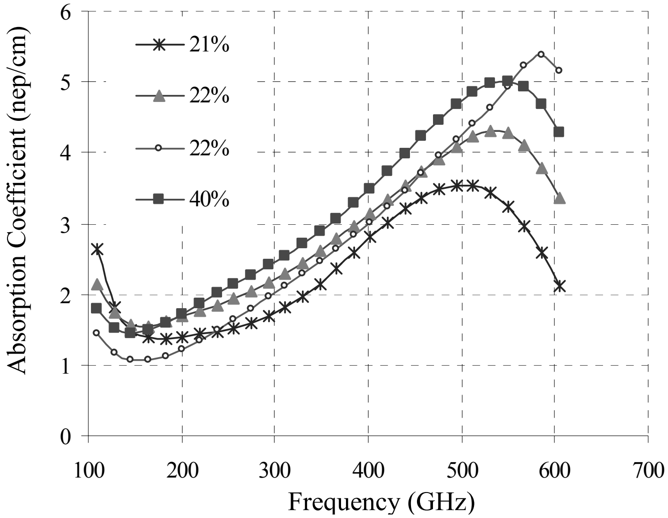

Figure 5: Absorption coefficient for different volume percent of Titania particles.

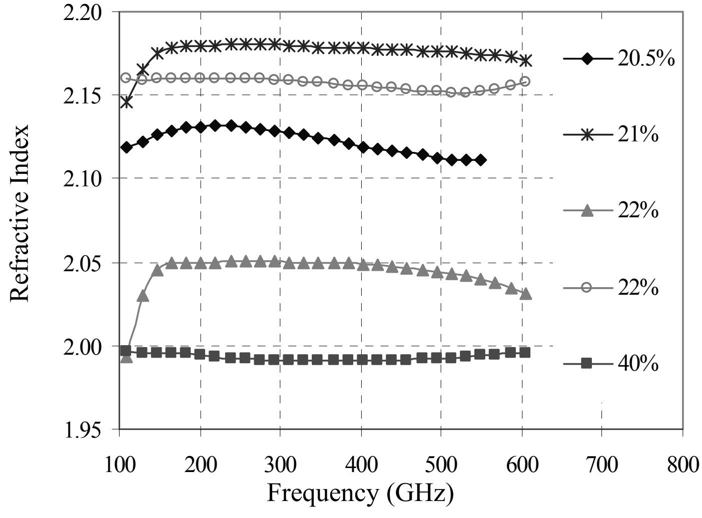

Figure 6: Refractive index for different volume percent of TiO_2.

Results obtained by using DFTS technique are shown in Figures 5, 6 and 7.

Figure 5 shows the absorption coefficient for different volume percents of Titania particles obtained by using the DFTS technique. The absorption coefficient of the sample with 40 volume percent of Titania particle is observed to be higher as compared to samples with 21 and 22 Titania volume percent.

Figure 6 shows the refractive index for different volume percent of Titania particles. Sample with 40 volume percent Titania shows the lowest refractive index. As the volume percent increases, the tendency for agglomeration of particles increases. If the agglomerated particle size is larger than half the wavelength of the incident light, then it will not scatter the light effectively which leads to poor refraction.

The agglomeration of TiO_2 particles in the scattering media is one example of a general phenomenon known called "dependent scattering": the light scattered by a unit concentration of scattering particles depends on the concentration of the scattering particles, scatter light which passes both inside and outside of their physical boundaries. In a concentrated suspension, these scattering volumes overlap, so that each particle "receives" less light than it is capable of scattering [8].

At low particle concentrations, the relationship between concentration and opacity is linear: doubling the concentration doubles the opacity. At higher TiO_2 concentrations, this is no longer the case. Crowding lowers the scattering power so that a significant increase in the TiO_2 concentration may result in very little increase in opacity. Indeed in some cases increasing concentration above certain point decreases the opacity. Clearly, the scattering efficiency of unit volume of TiO_2 is dependent upon the concentration of TiO_2 [9].

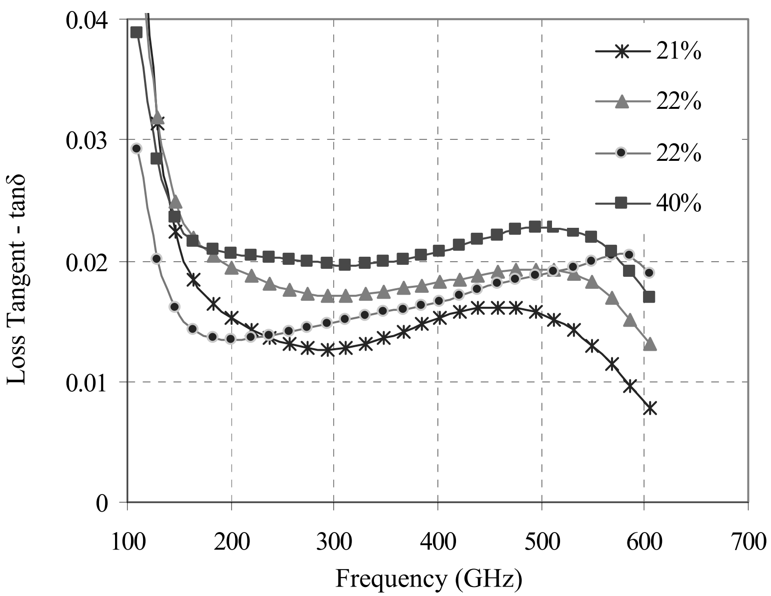

Figure 7: Loss tangent for different volume percent of TiO_2 particles.

Values of refractive index (~2.05 and 2.15) and absorption coefficient is significantly different for the samples with same the volume percent (i.e. 22%) of Titania particles, which can be attributed to the processing conditions of the sample and particle size distribution.

Figure 7 shows the loss tangent data measured for all the samples over the range of 100 - 600 GHz using the DFTS technique. Dielectric loss tangent is the ratio of imaginary permittivity to real permittivity, and determines how much energy is lost by the electromagnetic wave while passing through the medium. Small loss tangent indicates high-energy loss while large loss tangent indicates low energy loss. As expected, loss tangent for the sample with 40 volume percent is high (~0.02) as compared to all other samples because the large volume percent of the TiO_2 particles creates a barrier for the energy passing through the medium.

4 Conclusions

Dielectric properties, including complex permittivity, refractive index and loss tangent of the composite material have been studied in the millimeter wave frequency range. The measurements have been performed by using a high power free space quasi-optical spectrometer in the 44–90 GHz frequency range and a Dispersive Fourier Transform Spectrometer in the range of 100–600 GHz. Very low level of losses of millimetre wave radiation has been observed for composite samples. In addition, it is observed that the absorption coefficient and the loss tangent increases while the refractive index decreases as the volume percent of Titania particles increases in the composite materials from 20–40%.

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