

Terahertz absorption characteristics of guar gum determined via microfluidic technology

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Research

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Abstract

The vibrational energy levels of many biomolecules correspond to the terahertz band; thus, terahertz technology can be used to identify these substances. Moreover, as the biological activity of most biomolecules can be observed only in aqueous solution, the characteristics of such biomolecules must be studied in aqueous solution. In this study, a simple microfluidic chip, a temperature control device and a strong electric field device were designed to study the terahertz absorption characteristics of guar gum for different temperatures, concentrations and electric field exposure durations, thus enabling the use of terahertz technology to analyse the characteristics of guar gum.

Introduction

Electromagnetic waves in the terahertz (THz) band have a frequency range of 0.1–10 THz and a wavelength range of 0.03–3 mm. Studies have shown that the characteristic vibration modes of many biological macromolecules correspond to the THz band [1]; consequently, THz waves can be used to detect biological molecules [2-6]. Water plays an important role in the function of biomolecules, and thus, most experiments are performed in the solution state. Interactions among hydrated molecules in solution involve multiple biological phenomena [7], which are often denoted as hydration. Based on this principle, Yang et al. measured the spectrum of L-asparagine and L-asparagine monohydrate via THz time domain spectroscopy (THz-TDS) technology. In addition, he also observed dynamic changes in L-asparagine thermal dehydration in real time and found that THz waves are highly sensitive to changes in the crystal structure, the condition of the solution in which the crystal is contained and weak interactions between molecules [8]. Microfluidics, also known as lab-on-a-chip or microfluidic chip technology, enable researchers to precisely control and manipulate micro-scale fluids with submicron structures. Thus, microfluidics have practical value for distinguishing similar substances and detecting trace samples. Fisher et al. [9] measured the optical constants of four nucleotides in the THz band using THz technology and successfully identified these nucleotides. Serita et al. developed a THz microfluidic chip based on a nonlinear optical crystal, comprising an array of several split ring resonators, for the detection of ultra-trace biological samples [10] Baragwanath et al. used THz-TDS to examine a microfluidic chip and found that the time domain spectrum, refractive index and other parameters differed greatly for different concentrations and substances [11]. Thus, THz spectroscopy technology is a powerful tool for distinguishing substances and studying their structures.

Guar gum is an emulsifier, curing agent and stabiliser. Guar gum can act as a thickening liquid, can increase viscosity and reduce ice crystal formation, and is used in most processed foods. In this study, THz technology and microfluidic approaches were combined to study the THz absorption characteristics of guar gum for different concentrations, temperatures and electric field treatment durations. The method presented herein provides a feasible approach for rapidly identifying colloids.

Properties of guar gum

The molecular structure of guar gum is shown in Fig. 1 [12]. Guar gum is extracted from the endosperm of the leguminous plant guar bean as a free-flowing powder. The powder is generally white to light yellowish brown in colour and is nearly odourless. Guar gum is composed of approximately 75%–85% polysaccharide, 5%–6% protein, 2%–3% fibre and 1% ash.

Guar gum is a non-ionic neutral polysaccharide, with D-mannose linked by a β -1,4 bond as the main chain and D-galactose linked at the α -1,6 position as the branch chain. In general, the molar ratio of galactose to mannose is 1:2. The spatial structure of the plant is a curled spherical structure, with mannose on the inside and galactose on the outside. The ratio of mannose to galactose varies slightly for different plant varieties.

Guar gum [12] is a type of water-soluble natural polymer, which can be quickly hydrated in cold or hot water to obtain a translucent viscous liquid. The viscosity of a guar-gum-containing aqueous solution reflects the molecular weight of guar gum, while the swelling rate reflects the degree of difficulty that is encountered in swelling in guar gum applications. Higher temperatures can accelerate the swelling of guar gum, weaken the hydrogen bonding between molecular chains, increase the elongation of molecular chains and reduce the viscosity.

Notably, guar gum can form a high-viscosity aqueous solution at low concentrations [12] due to entanglement between polymer chains and intramolecular and intermolecular hydrogen bonding. The viscosity of 1% guar gum in aqueous solution is approximately 4000–6000 MPa•s. In addition, guar gum aqueous solutions exhibit typical winding polymer characteristics, corresponding to the pseudoplastic fluid characteristics of a non-Newtonian fluid, with no yield stress. Because guar gum is widely utilized and exhibits a high viscosity and rheological properties in natural rubber, the THz absorption of guar gum was studied in this work, with guar gum acting as a representative colloid for further experimental research.

Experimental system

Experimental light path

An in-house-built THz-TDS system was employed in this work. The light source is a self-mode-locked fibre femtosecond laser purchased from Peking University, with a central wavelength of 1550 nm, pulse width of 75 fs, pulse repetition rate of 100 MHz and power of 130mW. After passing through a polarising beam splitter prism, the output laser is divided into two beams. One beam is used as the pump light, which is coupled into a fibre-optic photoconductive antenna (BPCA-100-05-10-1550-c-f, BATOP Company) through a mechanical translation stage to generate a THz wave. The other beam is used as a detection beam, which is coupled into another fibre-optic photoconductive antenna (BPCA-180-05-10-1550-c-f of BATOP Company) to detect THz waves. The fabricated microfluidic chip is placed between two off-axis parabolic mirrors. The THz wave emitted by the THz antenna passes through the microfluidic chip filled with guar gum, is received by the detection antenna and is then input into the lock-in amplifier for amplification.

Next, the data are collected and processed by a computer. A schematic of the experimental optical path is shown in Fig. 2.

Fabrication of the microfluidic chip

THz microfluidic chip materials should exhibit high transmittance and allow for ease in processing. Currently, microfluidic chips are generally made of quartz glass, polydimethylsiloxane (PDMS) or polyethylene (PE). However, due to the low transmittance of quartz glass and PDMS for THz waves and the opacity of PE to visible light, these materials do not allow one to observe changes in liquid samples in a channel in real time. The transmittance of the cycloolefin copolymer Zeonor 1420R used in this study exceeds 90% and displays no obvious peaks, as shown in Fig. 3, which is suitable for the preparation of THz microfluidic chips.

The microfluidic chip in this study is a sandwich structure, with a 50- μm -thick strongly adhering double-sided adhesive as an interlayer and a concave microfluidic channel carved in the middle. The substrate and cover are composed of Zeonor 1420R material. A diagram of the process for preparing the microfluidic chip is shown in Fig. 4. In this study, we first measured the THz transmission characteristics of the microfluidic chip during continuous heating without liquid injection in order to assess the THz transmission characteristics of the chip under varying temperature. The results show that the transmission characteristics of the chip are not affected by temperature and that there is no leakage phenomenon. Therefore, the chip is suitable for the detection of liquid samples at different temperatures.

Temperature control system

To control the temperature of the guar gum, a high-precision temperature control system was designed. First, the fabricated microfluidic chip was bonded to a 2-mm-thick iron sheet by using a thermal conductive silica gel. A 6-mm-diameter hole was created on the iron sheet for THz waves to pass through. Second, a temperature sensor was secured to the same side of the iron sheet using thermal conductive silica gel. A circular alumina ceramic heating plate with holes (outer diameter: 40 mm; inner diameter: 10 mm) was glued to the other side of the iron sheet using thermal conductive silica gel in order to heat the microfluidic chip. The heating plate and temperature sensor were controlled by a temperature controller (ST700 intelligent PID temperature controller; temperature adjustment range: 0–400 °C; rated voltage: 220 V; working frequency: 50–60 Hz). The temperature controller, which is shown in Fig. 5, can adjust the temperature with an accuracy of 0.1 °C.

External electric field device

A schematic diagram of the external electric field device utilised in this experiment is shown in Fig. 6. A high-voltage power supply (dw-p153-05c51) was used to provide power. A uniform electric field was generated by two parallel metal plates, with a magnitude of approximately 2500 V/cm. The microfluidic chip was placed between the two metal plates for electric field treatment; subsequently, the two metal

plates were removed, and the transmission of the microfluidic chip was measured by the THz-TDS system.

Experiments And Results

Temperature characteristics

In this experiment, guar gum was prepared by adding 0.01 g guar gum powder to 500 mL deionised water; then, the mixture was stirred evenly and heated in a water bath for 2 min, resulting in 0.002% guar gum solution. When the colloid was irradiated with a laser pen, an obvious Tyndall effect was observed, indicating that the solution was a sol. The microfluidic chip was filled with the guar gum solution and placed between off-axis parabolic mirrors to conduct a transmission test using the THz-TDS system. The transmittance at room temperature (25 °C) was measured first, followed by the transmittance at 30 °C to 70 °C, measured in increments of 10 °C. When the temperature reaches 60 °C, the colloid inside the chip produces bubbles due to the temperature rise, and the measured signal fluctuates. To reduce the influence of bubbles on the measured signal, guar gum solution was continuously injected into the microfluidic chip when bubbles occurred during the heating process, and the solution was injected until the bubbles in the chip were eliminated. In this process, the colloid in the chip heats rapidly. When the guar gum solution reaches the target temperature, there are fewer bubbles in the water, which will not affect the analysis of the measured data. The THz time domain spectrum of guar gum is shown in Fig. 7, and the spectrum obtained by Fourier transform spectroscopy is shown in Fig. 8. The results shown in these figures demonstrate that the THz transmission intensity of guar gum decreases with increasing temperature, indicating that the THz absorption of guar gum increases with increasing temperature in the range of 25 °C–70 °C.

Concentration characteristics

Three concentrations of guar gum solution (0.1%, 0.3% and 0.4%) were prepared with deionised water. The THz frequency spectra for these solutions are shown in Fig. 9. These results indicate that a higher concentration of guar gum solution corresponds to a lower THz transmission intensity, resulting in a stronger THz absorption.

Characteristics under an applied electric field

The 0.002% guar gum solution was injected into the microfluidic chip, and the THz spectrum was obtained via the THz-TDS system without an electric field. Then, an electric field of 2500V/cm was applied parallel to the microfluidic chip, and the guar gum solution was placed in the electric field for 5 min. The power supply was then disconnected, the electrode plate was removed, and the THz spectrum was obtained with the THz-TDS system. Next, the microfluidic chip was shaken to return the sample to the original state as much as possible, the sample was placed in the electric field for 10 min, and the THz spectrum was obtained again. The THz spectra obtained in these three measurements are shown in Fig.

10. The results show that the THz transmittance increases with an increasing duration of electric field exposure, implying that the THz absorption intensity of the guar gum solution decreases.

Discussion

The THz spectra of guar gum solution at varying temperatures show that the THz transmittance decreases with increasing temperature. This result occurs because the outer layer of hydroxyl, alkoxy and oxygen atoms in glycoside bonds in guar gum molecules containing sp^3 hybrid orbitals. The unshared lone electron pairs in the orbitals can combine with partially positively charged hydrogen in the water molecule to form hydrogen bonds through electrostatic attraction [13]. Due to the stretching of guar gum molecules, a variety of groups are fully exposed. The polar groups and polar water molecules interact with each other by hydrogen bonding or dipole forces to form an inner-layer water film. The inner-layer water reacts with the outer-layer water to form an association. The sol molecules with a large volume act as the skeleton, a large amount of water is bound, and free movement of the medium is hindered, resulting in resistance between laminar flows. This resistance is exhibited as apparent viscosity, which causes the solution to display a quantitative viscosity [14]. When the temperature rises, the rate of molecular motion gradually increases, and the aggregates change from large to small. With an increase in absorbed energy, the structure of the system breaks down, and the viscosity decreases. In this process, the oxidative degradation of guar gum molecules leads to hydrogen bond breaking [14], and the THz transmission intensity should be enhanced. However, guar gum solution is a polar liquid in which dipole interactions occur. The absorption coefficient of polar liquids is larger in the THz range approximately 10–100 times that of non-polar liquids [15]. Therefore, the vibration between dipole molecules is the main reason that the THz absorption of guar gum increases with increasing temperature.

The THz transmission spectra of guar gum solution for varying concentrations (Fig. 9) show that the transmission intensity of THz waves decreases with increasing concentration; consequently, the THz absorption of guar gum solution increases. This result is due to the existence of hydrogen bonds between the guar gum molecules. An increase in the guar gum concentration leads to a higher number of hydrogen bonds, which in turn increases the absorption of THz waves. In addition, the vibration interactions between dipole molecules in the polar guar gum liquid also contribute to the increased THz absorption [15].

The THz transmission spectra of guar gum solution exposed to an electric field for varying durations (Fig. 10) indicate that a longer exposure to an electric field results in a higher THz transmission intensity for guar gum solution. This result occurs because the applied electric field can reduce hydrogen bonding and increase the diffusion coefficient of water molecules [16]. Therefore, it can be preliminarily concluded that the external electric field reduces the effect of hydrogen bonds in the sample, which increases the THz transmission; thus, the THz absorption intensity decreases as the duration of external electric field exposure increases.

Conclusion

In this paper, a new method for fabricating a THz microfluidic chip is proposed. A double-sided adhesive was used as the channel interlayer of the microfluidic chip, which greatly shortens the fabrication time and resolves the issue of chip leakage. A high-precision temperature control system was designed to control the temperature of guar gum solution, and a high-voltage power supply was used to provide a strong electric field. The THz transmission characteristics of guar gum solution were measured for different temperatures, concentrations and electric field exposure durations via a THz-TDS system, which indirectly reflected the THz absorption characteristics of guar gum.

The results show that the transmission intensity of THz waves in guar gum solution decreases with increasing temperature and concentration. This phenomenon was attributed to the viscosity of guar gum, the number of hydrogen bonds in solution and the vibration of dipole molecules. In addition, as the duration of electric field exposure increased, the THz transmittance of the guar gum solution increased, which was attributed to hydrogen bonds. This study expands the potential applications for THz technology and lays a foundation for the study of colloidal properties using THz methods.

Abbreviations

PBS: polarisation beam splitter; PCA: Photoconductive Antenna; PID: Proportion Integration Differentiation.

Declarations

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Authors' contributions

All authors contributed to the theoretical analysis, calculations, experiment and preparation of the manuscript.

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Figures

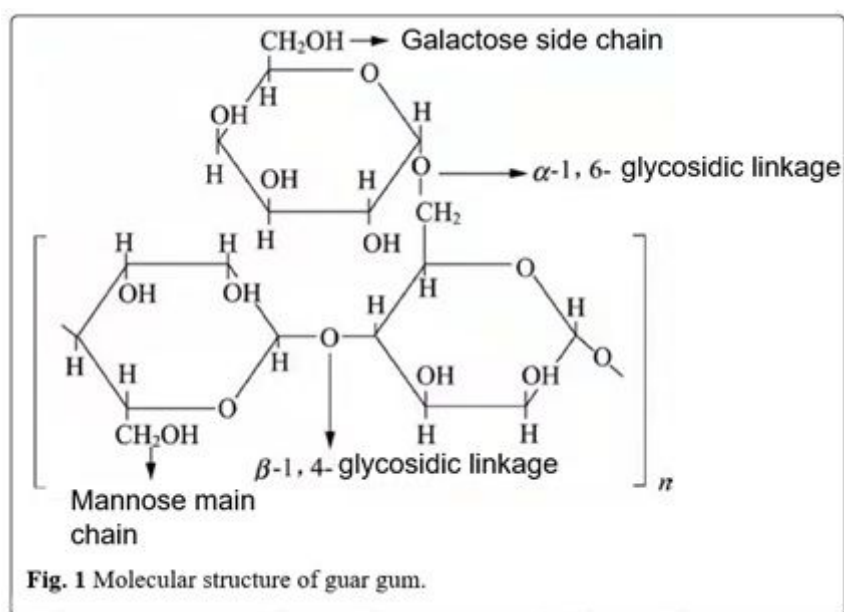


Figure 1

(see figure file for caption)

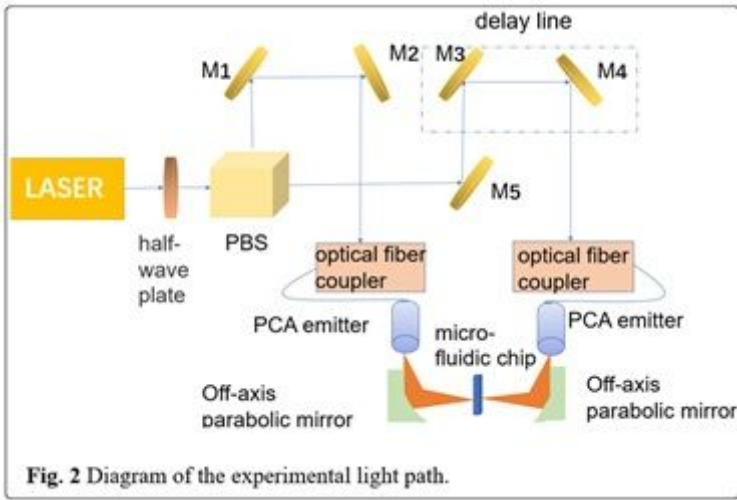


Figure 2

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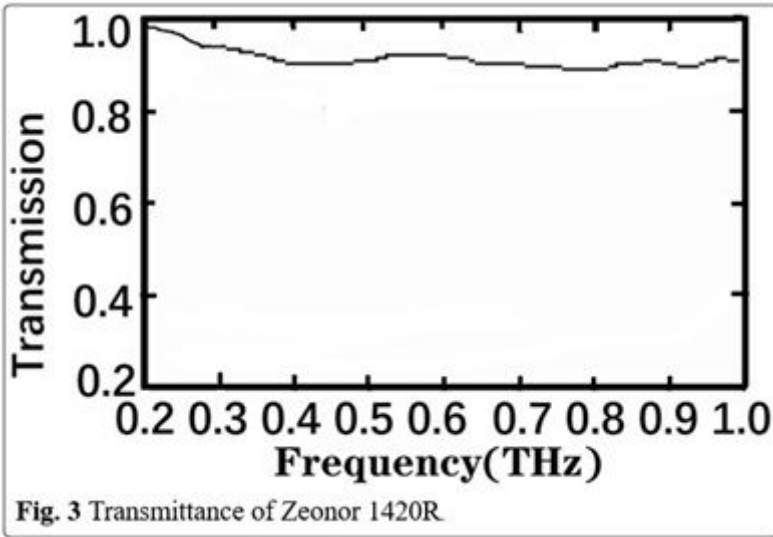


Figure 3

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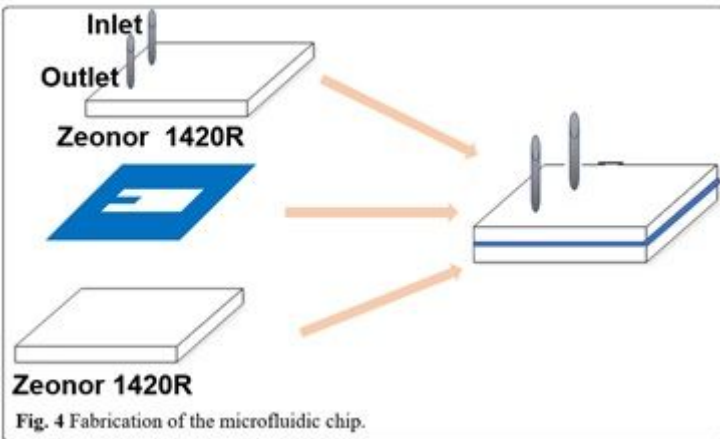


Figure 4

(see figure file for caption)

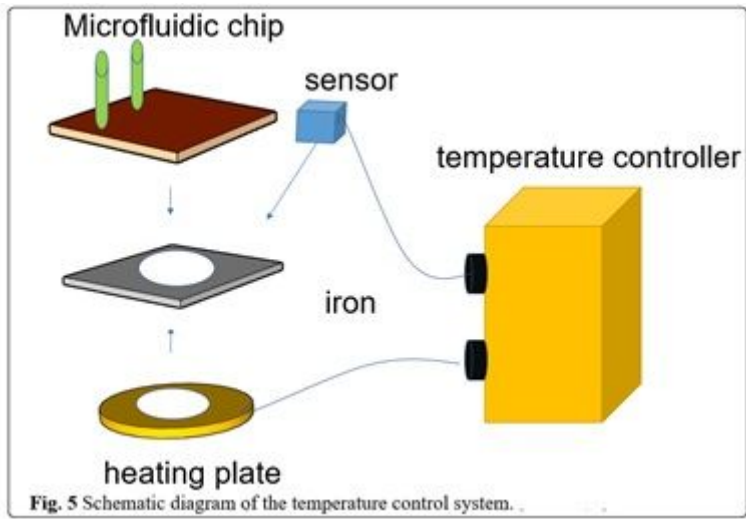


Figure 5

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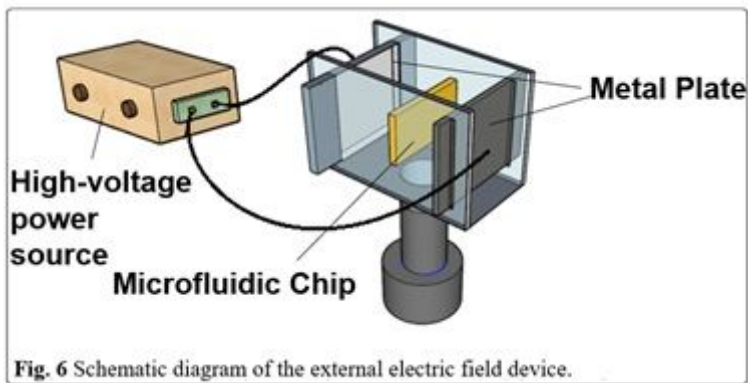


Figure 6

(see figure file for caption)

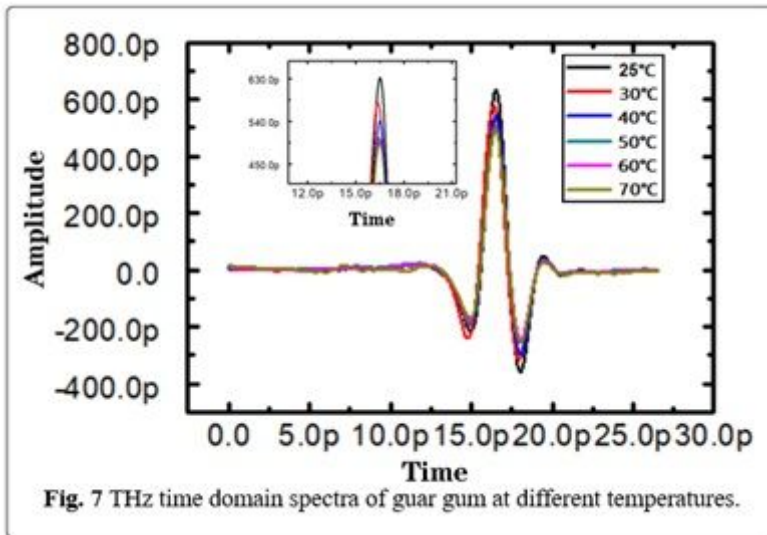


Figure 7

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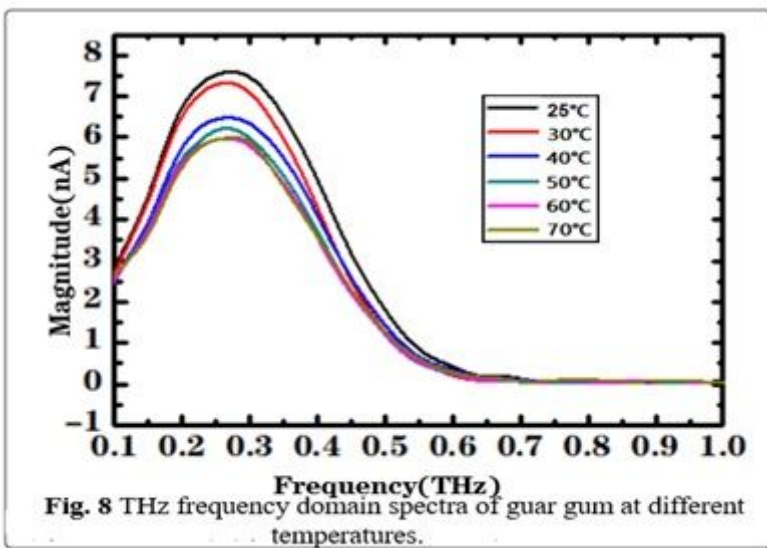


Figure 8

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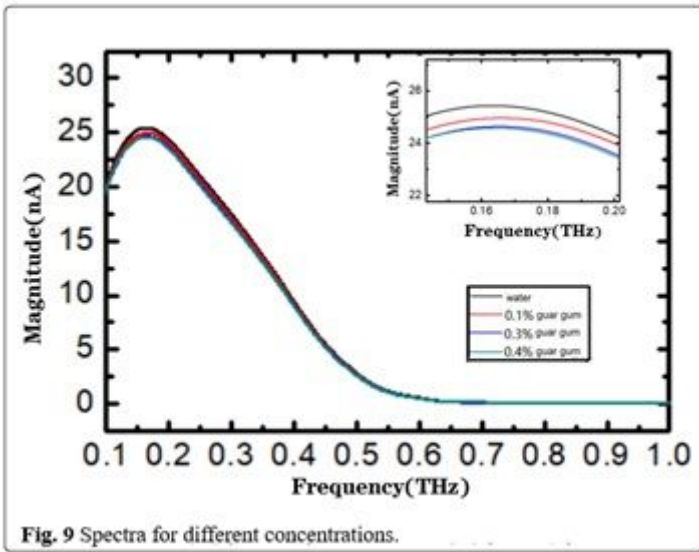


Figure 9

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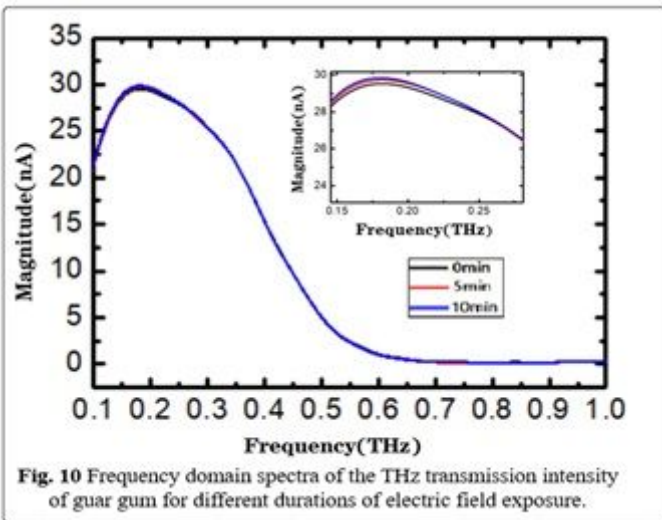


Figure 10

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