

# Fourier Transform Infrared Spectroscopic and AC Electrical Conductivity Studies of Chitin and Its Derivatives

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**ABSTRACT:** The vibrational modes and the purity index of chitin and its derivatives as biopolymers are studied by Fourier transform infrared spectroscopy in the wavenumber range from 4000 to 400  $\text{cm}^{-1}$ . The absorption bands of chitin and its derivatives are assigned. New bands appeared at 1419, 1209, 915, and 800  $\text{cm}^{-1}$  for chitin derivatives due to the change of vibrational modes. The purity indexes are calculated from the ratio of the absorption band of C = O at 1662  $\text{cm}^{-1}$  and OH at 3443  $\text{cm}^{-1}$ . Generally, the purity indexes of chitin derivatives are higher than that of chitin, which is due to the decrease of OH. The dielectric properties such as the real part of the dielectric constant ( $\epsilon'$ ) and loss tangent  $\tan(\delta)$  are measured as a function of temperature at

different frequencies ranging from 200 to 2000 kHz. The increase of ( $\epsilon'$ ) and  $\tan(\delta)$  with increasing temperature is discussed on the basis of increasing polarizability and the decrease with increasing frequency can be attributed to the dielectric dispersion. AC electrical conductivities as a function of the reciprocal of the absolute temperature are also discussed. The mechanism of the charge carrier is discussed as a tunneling model in the temperature range from 300 to 360 K. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 936–943, 2005

**Key words:** biopolymer; FTIR; structure; dielectric properties

## INTRODUCTION

Chitin is a high-molecular-weight linear polymer of *N*-acetyl-D-glucosamine (*N*-acetyl-2-amino-2-deoxy-D-glucopyranose) units linked by  $\beta$ -1, 4 bonds.<sup>1–3</sup> It is a highly insoluble material with low chemical reactivity. It may be regarded as cellulose with the hydroxyl at position C-2 replaced by an acetamido group. Like cellulose, it naturally functions as a structural polysaccharide. It is most abundant in crustaceans, insects, and fungi. Chitin is a white, hard, inelastic, nitrogenous polysaccharide and the major source of surface pollution in coastal areas.<sup>3,4</sup> Chitin is of commercial interest due to its high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%); this makes chitin a useful chelating agent.<sup>5</sup> As most polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as chitin and its derivatives.<sup>6</sup> In this respect, chitin is recommended as a suitable resource material, because natural polymers have excellent properties such as nontoxicity, adsorption, and so on. Chemically modified chitin structures, resulting in improved solubility in general organic

solvents, have been reported by many workers.<sup>5–7</sup> Chitin is a highly basic polysaccharide and its unique properties include polyoxysalt formation, ability to form films, chelation of metal ions, and optical structural characteristics. Hydrolysis of chitin with concentrated acids under drastic conditions produces a relatively pure form of the amino sugar D-glucosamine.<sup>8</sup> The interest in chitin originates from the study of the behavior and chemical characteristics of lysozyme, an enzyme present in human body fluids.<sup>9</sup> Chitin has many distinctive biomedical properties and has been applied in many different industrial areas.<sup>10</sup> Chitin can be N-deacetylated to such an extent that it becomes soluble in dilute aqueous acetic and formic acids.<sup>11</sup>

Dielectric constant measurement is a well-established tool in the investigation of synthetic polymer materials. Many review articles<sup>12–16</sup> deal with this subject, presenting theoretical and experimental aspects and summaries of many experimental data of this substance class. On other hand, the dielectric and dynamic properties of polysaccharides have also been discussed,<sup>17,18</sup> although in general, the dielectric constant of polysaccharides has been considered controversial by many scientists up to now. Polysaccharides consist of anhydroglucose units, carrying two hydroxyl groups (-OH) and one methylol group (-CH<sub>2</sub>-OH). Dielectric relaxation separates different molecu-

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lar groups of a repeating unit of a polymer with respect to the rate of its orientational dynamics.<sup>19</sup>

The aim of the present work is to use the chemical processes to separate chitin and treat it with some chemical properties. The improvements of such properties will open a new era for chitin to be more applicable in drug manufacture. FTIR, AC conductivity, and dielectric constant are the most important parameters to detect how chitin is improved.

## EXPERIMENTAL

Chitin was prepared from shrimp shell by the procedure described in the literature.<sup>20</sup> Chitin phosphate, chitin sulfonate, chitin carboxylate, and chitin phosphosulfonate were prepared according to the method previously reported.<sup>21</sup> Five grams of chitin was suspended in cooled 50 mL pyridine; 5 mL of POCl<sub>3</sub> or ClHSO<sub>3</sub> in 25 mL of methylene chloride was added to the chitin solution in pyridine dropwise. The reaction mixture was cooled in an ice bath for 3 h. The contents of the flask were poured into ice water, filtered, washed with deionized water followed by HCl and then with deionized water till neutrality, and finally dried in air. Details of the phosphosulfonation are given elsewhere.<sup>22</sup>

A Jasco Model 300E Fourier transform infrared spectrometer was used to measure the vibrational spectra of the investigated samples. The samples were measured using the KBr disc technique. Measurements of the AC conductivity were carried out on samples in the form of a disc of about 1 cm diameter and 0.16 cm thickness. The two surfaces of each sample were coated with silver paint (BDH) and checked for good contact. The dielectric constant was carried out from room temperature up to 440 K as a function of frequencies ranging from 200 to 2000 kHz using an RLC bridge (HIOKI Model 3530, Japan). The accuracy of measurement for both parameters was less than 3%. An Oxford high vacuumed cryostat with intelligent controller (ICT 503) was used for measuring the AC conductivity and dielectric constant.

The dielectric constant ( $\epsilon'$ ) was measured using the relation  $\epsilon' = \frac{Cd}{\epsilon_0 A}$  where  $C$  is the capacitance of the sample,  $d$  is the thickness,  $A$  is the surface area, and  $\epsilon_0$  is the permittivity of free space  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m. The tangent of the dielectric loss angle  $\tan(\delta)$  was measured directly from the bridge, where  $\tan(\delta) = \epsilon''/\epsilon'$ .

## RESULTS AND DISCUSSION

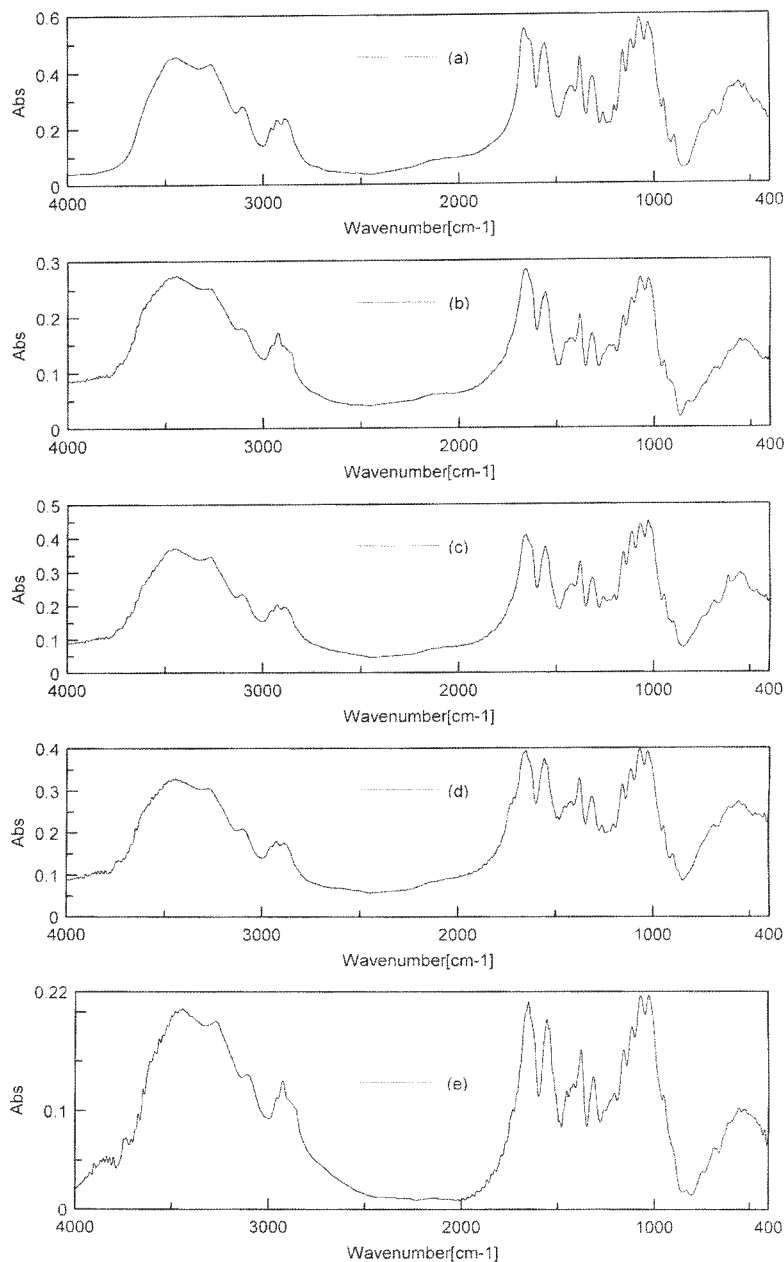
### Infrared spectroscopy

The infrared absorption spectra of chitin, phosphorylated chitin, sulfonated chitin, carboxylated chitin, and

phosphosulfonated chitin are shown in Figure 1a–e. Fig. 1a shows that broad OH stretching vibration bands appeared at 3443 cm<sup>-1</sup>. The NH symmetric and asymmetrical stretching vibration bands appeared at 3266 and 3105 cm<sup>-1</sup>, respectively. The CH symmetric and asymmetric stretching vibrations of CH<sub>2</sub> groups were observed at 2959, 2928, and 2889 cm<sup>-1</sup>, respectively. The spectral region of 850–1700 cm<sup>-1</sup> is the information-rich region. The faint absorptions at 1662 and 1558 cm<sup>-1</sup> are due to C = O bond and NH deformations, respectively. The absorption bands at 1428, 1378, and 1315 cm<sup>-1</sup> were attributed to CH<sub>2</sub> bending vibration, CH bending vibration, and CH<sub>2</sub> wagging, respectively. The bands appearing at 1261 and 1204 cm<sup>-1</sup> are due to NH bending vibration and OH in-plane bending. The absorption band appearing at 1158 cm<sup>-1</sup> is due to the asymmetric in-plane ring deformation. The absorption bands appearing at 1116, 1073, and 1026 cm<sup>-1</sup> are due to C-O and C-C stretching vibration. The two absorption bands at 949 and 896 cm<sup>-1</sup> are due to C-O ring vibration and ring bending.<sup>23</sup> The broad intense band at 1000–1220 cm<sup>-1</sup> was attributed to the ring and bridge C-O-C vibrations of chitin-ether-type absorption. On the other hand, a weak shoulder at 710 cm<sup>-1</sup> and well-resolved band at 693 cm<sup>-1</sup> are assigned to the out-of-plane bending of NH (amide) participating in hydrogen bonding formation, respectively.<sup>23</sup> The purity index of chitin is 1.769, which was determined from the absorbance ratio of C = O at 1662 cm<sup>-1</sup> and OH at 3443 cm<sup>-1</sup>.

To give clear information about the vibrational mode changes due to phosphorylation, sulfonation, carboxylation, and phosphosulfonation, the infrared spectra of chitin will be compared with its derivatives. From Fig. 1b it can be noticed that a new band appeared in phosphorylated chitin at 1209 cm<sup>-1</sup>, which is characteristic of the C-O-P bond. On the other hand, new bands appeared at 1419 and 810 cm<sup>-1</sup> in Fig. 1c. These bands are due to the sulfonated structure and are characteristic of the C-O-S bond. Also in Fig. 1d new bands appeared at 1420, 1205, and 815 cm<sup>-1</sup> due to carboxylation and are characteristic of the C-O-C bond. However, chitin phosphosulfonate gave new bands at 1419, 1206, and 915 cm<sup>-1</sup> in Fig. 1e, which are characteristic bands of the C-O-P and C-O-S bonds. Generally, the change of chitin structure due to phosphorylation, sulfonation, carboxylation, and phosphosulfonation is shown in Structure 1.

The purity indexes were determined for phosphorylated, sulfonated, carboxylated, and phosphosulfonated chitin from the absorbance ratio of C = O at 1662 cm<sup>-1</sup> and OH at 3443 cm<sup>-1</sup> and it gives the values 2.2, 2.4, 2.368, and 2.52, respectively. Generally, the purity indexes of chitin derivatives are higher than that of chitin. This can be attributed to presence of the amino group, which has a lower tendency to form hydrogen bonding with the OH group. This also indicates that



**Figure 1** Absorption spectra of chitin (a), chitin phosphate (b), chitin sulfonate (c), chitin carboxylate (d), and chitin phosphosulfonate (e).

extra hydrogen bonding from the amino group plays an important role in the purity value of chitin derivatives.

### Electrical studies

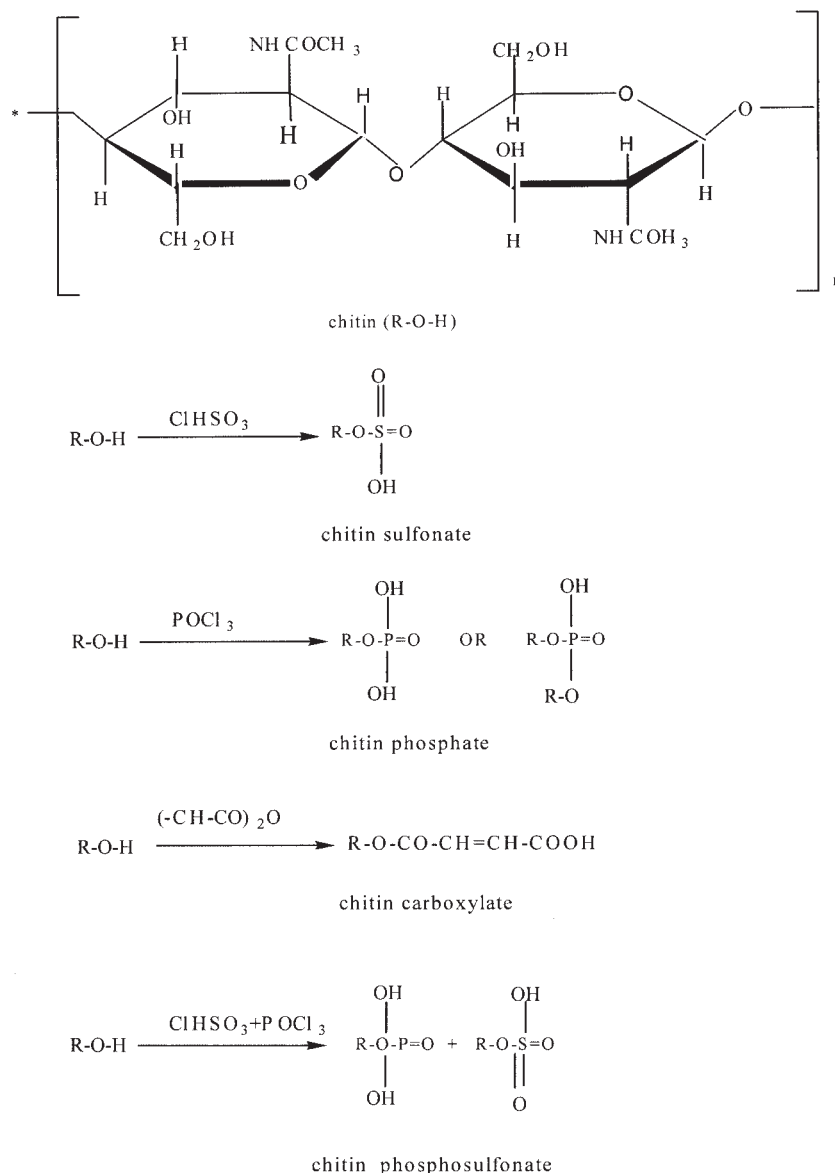
Real part of dielectric constant ( $\epsilon'$ )

The changes of the real part of the dielectric constant ( $\epsilon'$ ) for chitin and its derivatives (phosphorlated, sulfonated, carboxylated, and phosphosulfonated) with temperature from 340 to 440 K as a function of fre-

quency ranging from 200 to 3000 kHz are shown in Figure 2a–e. Figure 2a shows that ( $\epsilon'$ ) increases with increasing temperature, giving rise peak at 340 K, after which it decreases. The increase in ( $\epsilon'$ ) is due to the space charge polarization and dipole moments. Generally, the measured permittivity depends on the polarizability ( $\alpha$ ),

$$\alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_s, \quad (1)$$

where  $\alpha_e$ ,  $\alpha_a$ ,  $\alpha_d$ , and  $\alpha_s$  are the electronic, atomic, orientation (or dipole), and space charge (or interfa-



**Structure 1** Molecular structure of chitin and its derivatives.

cial) polarizability.<sup>24</sup> Also it can be calculated from the Clausius, Mossotti, and Debye equation (2).<sup>25-29</sup>

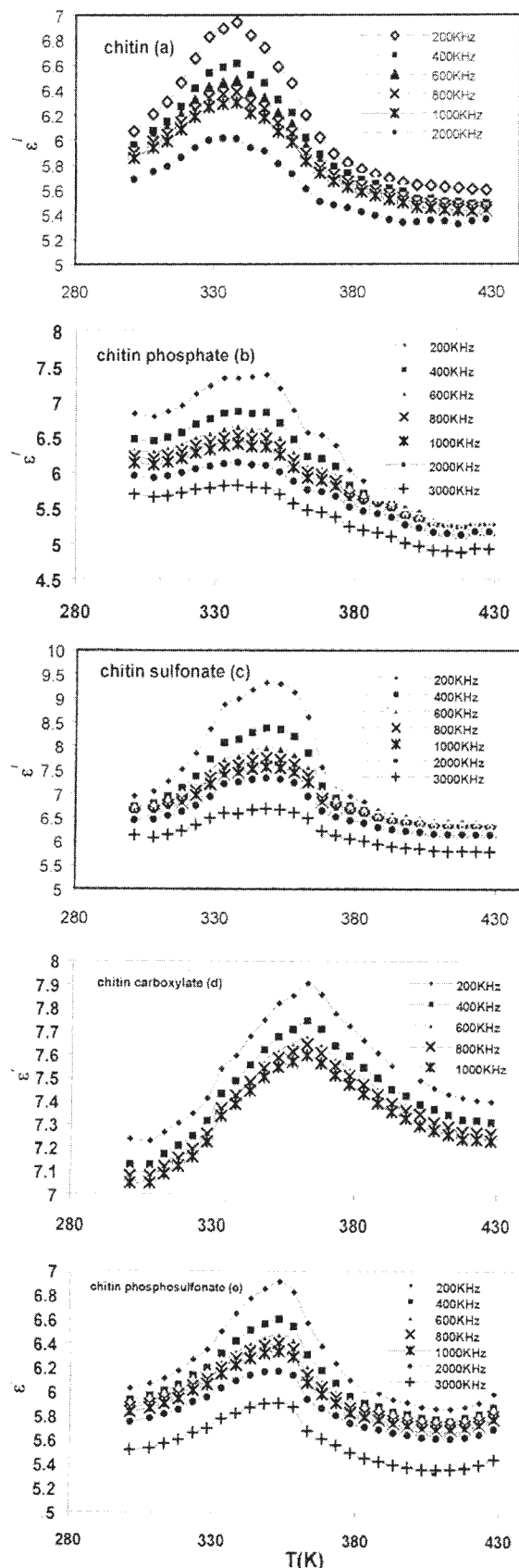
$$\frac{\epsilon' - 1}{\epsilon' + 2} = \frac{N\alpha}{3\epsilon_0 V'} \quad (2)$$

where  $N/V$  is the number density. In the case of polar dielectric, the electronic and ionic polarizability are replaced by the dipole polarization and are obtained<sup>30</sup>

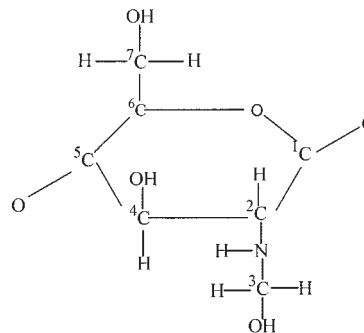
$$\frac{\epsilon' - 1}{\epsilon' + 2} \cdot \frac{M}{D} = \frac{N_A}{3\epsilon_0} \left[ \alpha + \frac{\mu^2}{3k_B T} \right] \quad (3)$$

where  $\mu$  = constant electric moment,  $k_B$  is the Boltzmann constant,  $T$  is the temperature of the sample, and

$M/D$  is the rate of molecule mass to density. So, from Eq. (3) the polarizability ( $\alpha$ ) appears to increase with increasing temperature. In the presence of an externally applied electric field, the molecules tend to orient themselves in the direction of the field.<sup>30</sup> In chitin we suggest a site model of the repeating unit of chitin, the anhydroglucose unit (AGU), wherein all relevant dipolar moments and all possible reorientation motions are labeled. The types of dipolar and movable sites in chitin are as follows: the pyranose ring is movable by orientational motions around the glucosidic bonds -O-, the side groups in the positions  $C_{(2)}$ ,  $C_{(3)}$ , and  $C_{(4)}$  have a rotation mobility around the C-N, C - O, and C-C linkages and  $C_{(5)}$  around the C-O linkage, also the  $C_{(7)}$  position has one mobility around



**Figure 2** Real part of the dielectric constant ( $\epsilon'$ ) of chitin (a), chitin phosphate (b), chitin sulfonate (c), chitin carboxylate (d), and chitin phosphosulfonate (e) as a function of temperature at different frequencies.



**Structure 2**

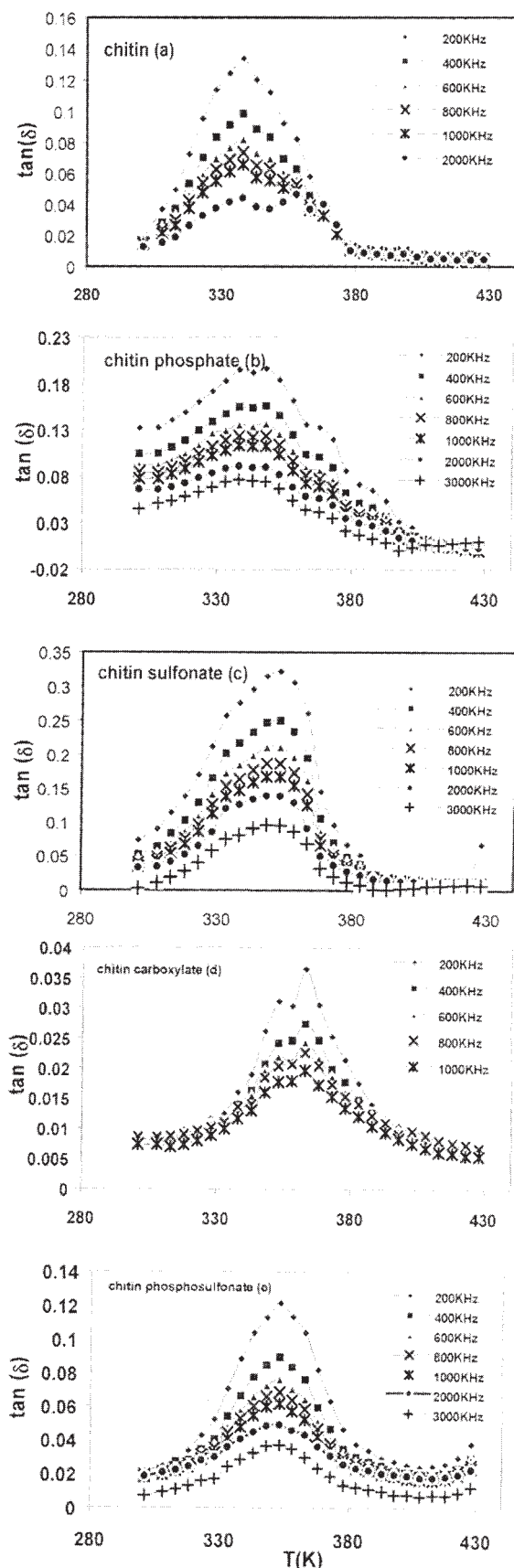
$C_{(6)}-C_{(7)}$  and an additional rotation mobility around the  $C_{(7)}-O$  linkage in Structure 2.<sup>31</sup> Generally, the polarizability ( $\alpha$ ) increases by increasing the dipolar moment, orientation, and reorientation motion, which is due to the increase of ( $\epsilon'$ ) with temperature up to 340 K. A distinct phase transition appears at 340 K; after that the real part ( $\epsilon$ ) decreases with increasing temperature. This characteristic of the orientationally disordered phase is observed and the thermal energy given to the sample is quite sufficient to disturb the aligned dipoles and interns; the polarization is decreased with the result of decreasing ( $\epsilon$ ). The slight decrease of ( $\epsilon'$ ) after 390 K may be due to the fact that molecules bound to the hydrophilic groups of the AGU, resulting in an increase of the dipolar moment of the side groups and affecting the polymer main chain dynamics.<sup>31</sup> Generally, the real part ( $\epsilon$ ) decreases with increasing frequencies and this can be attributed to the rapid alternation of the field accompanying the higher applied frequencies.

By comparing ( $\epsilon'$ ) of chitin and its derivatives in Figure 2b–e it is found that the phase transition is changed from one derivative to another and it appears at 345, 352, 360, and 355 K for phosphorlated, sulfonated, carboxylated, and phosphosulfonated chitin, respectively. This may be due to the change of the vibrational mode of the derivatives as shown in Structure 1.

#### Loss tangent ( $\tan(\delta)$ )

The variation of the loss tangent  $\tan(\delta)$  for chitin and its derivatives (phosphorlated, sulfonated, carboxylated, and phosphosulfonated) as a function of the applied frequencies (Fig. 3a–e) is similar to that of ( $\epsilon$ ) for the same samples. The only variation is in values that put the position of the peak nearly the same. The behavior of  $\tan(\delta)$  can be ascribed to some factors such as the decrease in the internal viscosity and the increase of the dipole fraction as well as the energy dissipation inside the sample. By comparing the loss tangent of chitin and its derivatives in Figure 3a–e it is





**Figure 3** Dielectric loss  $\tan(\delta)$  of chitin (a), chitin phosphate (b), chitin sulfonate (c), chitin carboxylate (d), and chitin phosphosulfonate (e).

found that the maximum peak position changes from one sample to another, which is due to the change of the chemical structure of chitin by its derivatives.

AC electrical conductivity

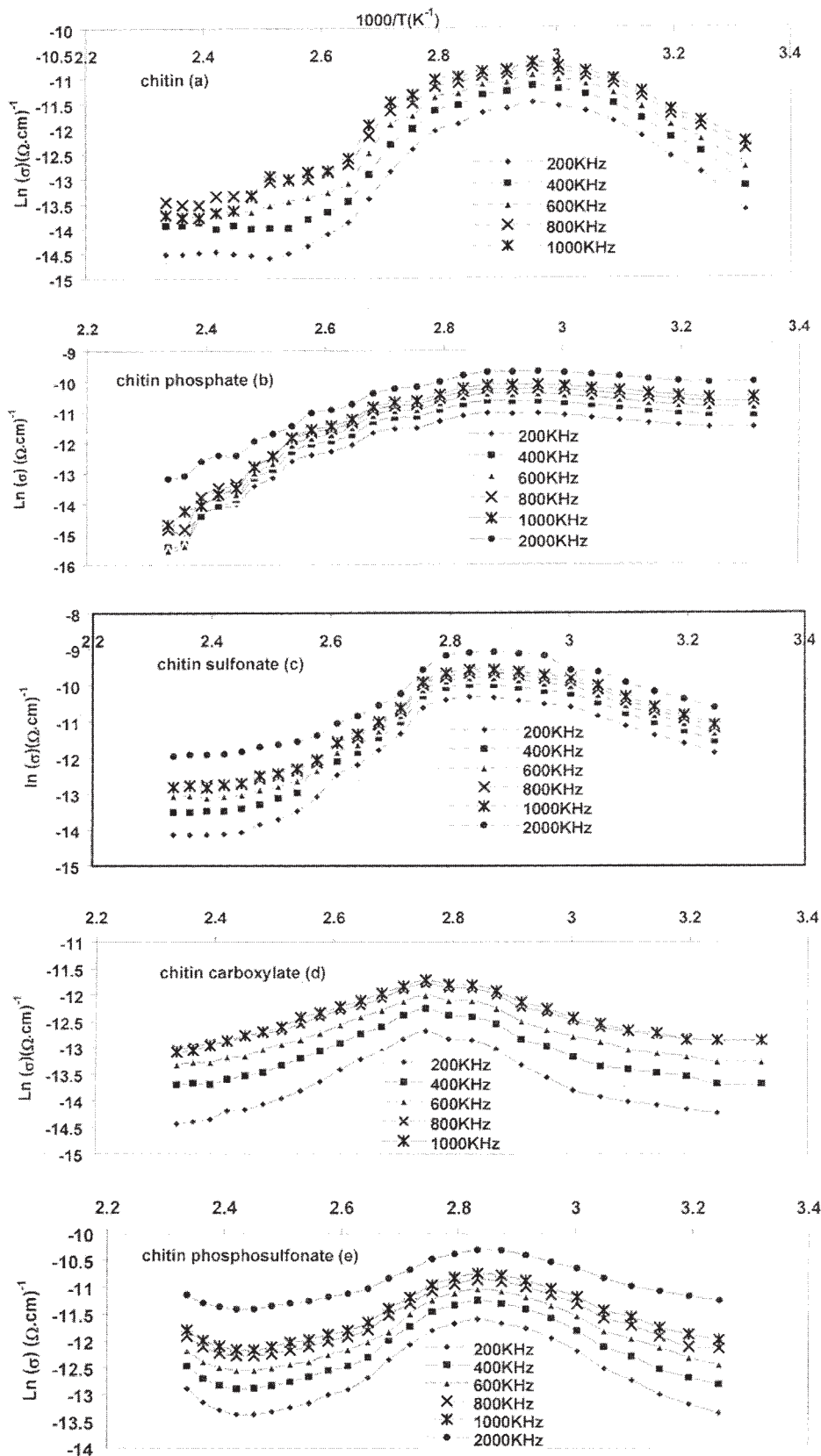
The dependence of AC electrical conductivity on the reciprocal of absolute temperature at different frequencies is shown in Figure 4a–e. Figure 4a shows that two different regions are observed for chitin. The first, in which conductivity increases with increasing temperature, is from 300 to 335 K. This behavior is acceptable because the thermal energy activates the charge carriers and increases their mobilities with the result of increasing conductivity up to the phase transition at 335 K. The tunneling model is applied in the mechanism of charge carriers, which assumes that an electron in a molecular orbital on one molecule, when excited to a higher energy level, can tunnel through a potential barrier to a nonoccupied state of a neighboring molecule with energy conserved in the tunneling process. The energy depends on the spin. Therefore, the electron in the excited state may tunnel to its neighbor molecule or return to its ground state, but in general, the probability for the lower state is much larger than that for the later state. Also, the conductivity has a frequency dependence that increases with increasing frequency. After  $T > 335$  K the conductivity decreases with increasing temperature and this may be due to the fact that the dipoles change from an ordered to a disordered state, which is called an order–disorder phase transition. The AGU ring plays a significant role in this process. The same trend of chitin derivatives is observed and the data can be divided into two main regions also. In the first region the electrical conductivity increases with the reciprocal of absolute temperature at all frequencies up to 345, 360, 365, and 357 K for phosphorlated, sulfonated, carboxylated, and phosphosulfonated chitin, respectively, due to an increase in the tunneling process. In general, the conductivity decreases with increasing frequency. The available experimental results on the frequency dependence of AC conductivity have revealed a considerable similarity of behavior for all derivatives. An empirical relation can express the frequency dependence of AC conductivity<sup>34,35</sup> as

$$\sigma_{AC} \propto (2\pi f)^n, \tag{4}$$

where  $n$  is not a constant for all substances, but it is a function of temperature, approaching unity at low temperatures and 0.5 or less at high temperature.

CONCLUSIONS

New bands appeared in FTIR spectra in the chitin derivatives due to the change of the vibrational mode.



**Figure 4** AC electrical conductivity of chitin (a), chitin phosphate (b), chitin sulfonate (c), chitin carboxylate (d), and chitin phosphosulfonate (e).

The purity indices were higher in chitin derivatives than those of chitin itself. The data of the dielectric constant and AC conductivity enhance the change of the vibrational modes.

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