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Molecular structure and dielectric properties studies of chitin and its treated by acid, base and hypochlorite

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Abstract

In this work, the chitin was treated by 0.1 N HCl, 0.5 N NaOH, and 8% sodium hypochlorite. The change of the molecular structure was studied by Fourier Transform Infrared Spectroscopy (FTIR) in the wavenumber range (400–4000 cm^{-1}). The absorption bands were assigned and the crystallinity index was calculated from the ratio of the absorbance C–N band at 1378 cm^{-1} and CH at 2925 cm^{-1}. The data indicated that, the crystallinity index of chitin is higher than that of treated chitin which is due to the hydrolysis of some acetamide group. Also, treating with alkali causes a swelling of chitin chains. The dielectric properties such as dielectric constant (ε'), dielectric loss (ε'') and AC electrical conductivity were measured and discussed as a function of frequencies (0.1 kHz–3 MHz). The dielectric constant (ε') was decreased with increasing frequencies due to the dielectric dispersion. β-relaxation was observed and discussed from the dielectric loss (ε''). The results of AC conductivity showed that, at high frequency, the conductivity increased with increasing frequencies and its interpreted in term of hopping conduction.

Keywords: Chitin acid; Chitin base; Chitin hypochlorite; FTIR and dielectric properties

1. Introduction

Chitin is one of abundant organic materials being second only to cellulose in the amount produced annually by biosynthesis. Chitin and chitosan are important polysaccharide extracted from different sources (craks, or shrimp shell, furg, etc.) (Rathke & Hudson, 1994). These polymers are composed of β–o-4 repeated glucosamine unit attached with a variable *N*-acetyl group along the polymeric backbone (Pangburn, Trescony, & Heller, 1988). The distribution of the *N*-acetyl groups along the polymeric backbone may control the solubility in a given solvent. When the average of the degree of acetylation (DA) is lower than 0.5, the polymers are called chitosan and becomes soluble in aqueous solution in presence of acid as acetic acid (Pariser & Lombordi, 1980). Chitin occurs naturally in three polymeric forms known as α, β, and γ chitin (Yalpani, Johnson, & Robinson, 1992). Chitin is a linear polysaccharide where chains are composed of 2-acetamido-2-deoxy-D-glucopyranose linked by β-(1 → 4) glucoside bonds and its idealized structure is shown in the structure of chitin (Yalpani et al., 1992).

Chitin is a white, hard, inelastic, nitrogenous polysaccharide and the major source of surface pollution in coastal areas (Muzzarelli, 1973, 1986). 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 (Austin, 1977). Chitin 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. The insolubility in solvent, except some special ones such as hexafluro-2-propanol, dimethylacetamide, HCl and trichloroacetic acid-dichloroethane (Kubita, Koyama, Nishamura, & Kamiya, 1989) had undoubtedly, delayed the basic and

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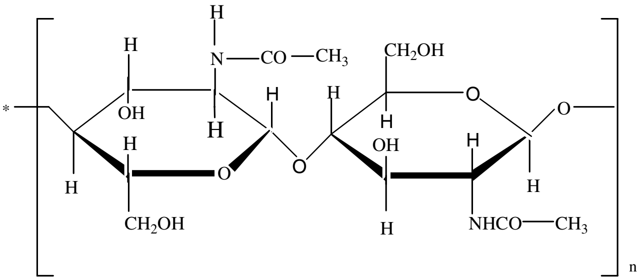


structure of chitin

utilization study of chitin (Rudall, 1963). The principle derivative of chitin is chitosan, generally produced by alkaline deacetylation of chitin. Chitin and chitosan are considered ecologically conservation materials on the earth and it have many practical applications. Chitin and chitosan have been investigated for practical applications such as biomedical and agricultural purposes. Natural chitin has strong hydrogen bonds in the molecules and the destruction of the hydrogen bonds and their reorganization give a rise gel (Mink & Blackwell, 1978). Hydrolysis of chitin with concentrated acids under drastic conditions produces a relatively pure form of the amino sugar D-glucosamine (Ravi Kumar, Rajakala Sridhari, Durga Bhavani, & Dutta, 1998). The interest in chitin originates from the study of the behavior and chemical characteristics of lysozyme, an enzyme present in human body fluids (Ravi Kumar, 1999). Chitin has many distinctive biomedical properties and has been applied in many different industrial areas (Ravi Kumar, 2000). Chitin can be *N*-deacetylated to such an extent, that it becomes soluble in dilute aqueous acetic and formic acids (Duarte, Ferreira, Marvao, & Rocha, 2002).

Dielectric constant is a well-established tool in the investigation of synthetic polymer materials. Many review articles deal with this subject, presenting theoretical and experimental aspects and summaries many experimental data for this substance class (Havriliak & Havriliak, 1996; Lindsey & Patterson, 1980; Roling, 1999; Sullivan & Deutsch, 1975; Burchard, 1983). On other hand, the dielectric and dynamic properties about polysaccharides was studied of some natural polymer (Gilbert, 1993; Franz, 1991). In general, the dielectric of polysaccharides has been considered controversial by many scientists, up till now. Polysaccharides consist of anhydroglucose units, carrying two hydroxyl groups (–OH) and one methylol group ($-CH_2-OH$). Dielectric relaxation separates different molecular groups of a repeating unit of a polymer with respect to the rate of its orientation dynamics (Einfeldt, Meibner, & Kwasniewski, 2003). In general, most of the polymers are insulators because of their low conductivity. The conductivity depends on the thermally generated carriers and also on the addition of suitable dopants (Mehendru, Pathak, Jain, & Mehendru, 1997; Shinka, Talmar, & Srivastava, 1989). Although, charge transport in polymers is a problem with great technological implication, the current understanding of the elemental processes involved is still unsatisfactory. Generally, polymers are amorphous or semicrystalline substances (Bassler, 1984). In amorphous substances there are many localized charge carrier levels called trapping sites and the carrier mobility is very low. The transport mechanism in amorphous materials is more complicated than in crystalline materials, where a long range order exists.

The aim of this work is to investigate the effect of acid, alkali and hypochlorite treatment on the molecular structure, and the electrical properties of chitin. The improvements of such properties for chitin and its derivatives will be more applicable in industry.

2. Experimental

Chitin was prepared from crab shell according to Zhang, Haga, Sekiguchi, and Hirans (2000). The prepared chitin was refluxed with 0.1 N HCl and 0.5 N NaOH for 2 h. Hypochloride treatment was prepared with 8% sodium hypochlorite solution at 65 °C for 2 h.

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.

The dielectric constant and AC electrical conductivity was carried out from 0.1 kHz–3 MHz using an RLC bridge (HIOKI model 3530) "Japan". The accuracy of measurement for both parameters was less than 3%. Oxford high vacuum cryostat with intelligent controller (ICT 503) was used for measuring the AC conductivity and dielectric constant.

The complex dielectric constant $\varepsilon^*(f, T) = \varepsilon'(f, T) - j\varepsilon''(f, T)$ or $\sigma^*(f, T) = \sigma'(f, T) + j\sigma''(f, T)$ results from the equivalent parallel circuit elements R and C of the measuring capacitor filled with the sample with help of the value of the empty capacitance. $C_o = \varepsilon_o A/d$ (area A and distance d of the plan parallel electrode system; ε_o-permittivity of the vacuum; imaginary unit $j^2 = -1$). $\varepsilon'(\omega)$ (dielectric store coefficient) is the real part and $\varepsilon''(\omega)$ (dielectric loss coefficient) is the imaginary part of the complex permittivity. $\varepsilon'(f, T) = c(f, T)d/\varepsilon_o A$, $\varepsilon''(f, T) = R^{-1}(f, T)d/\varepsilon_o \omega A$, the permittivity of free space $\varepsilon_o = 8.85 \times 10^{-12}$ F/m.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectra of untreated and treated chitin were recorded in the wavenumber region (400–4000 cm^{-1}) as shown in Fig. 1(a–d). The band appeared at about 3441 cm^{-1} is the characteristic of OH group. The two bands appeared at about 3256 and 3105 cm^{-1} were assigned to N–H symmetric and asymmetric stretching vibration of amide groups. These two bands were attributed to the vibrational mode of NH amide (intermolecular hydrogen bonding C=O···NH and H bonded NH group of chitin) (Pangburn et al., 1988). In general, characteristic

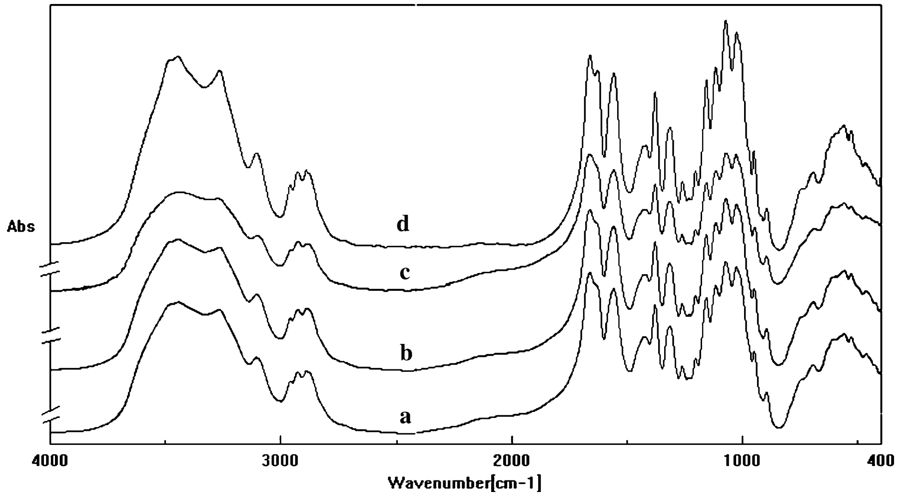


Fig. 1. FTIR spectra of (a) chitin, (b) chitin acid (c) chitin base (d) chitin Hypochlorite.

bands at 2959 and 2890 cm^{-1} represent the symmetric and asymmetric stretching vibration of aliphatic CH_2 group (Rathke & Hudson, 1994). The band appeared at about 1659 cm^{-1} was assigned to NH bending of amide groups and this band was used for determination of the residual amide group (–CO–NH–). The band around 1429 cm^{-1} was assigned to OH bending and is dependence on the favorable orientation of 1^{ry} OH group. The band at 1379 cm^{-1} represents the stretching vibration of amide N–C (Rathke & Hudson, 1994).

By comparing the spectra of untreated and treated chitin, it was found that, the *N*-deacetylation was associated with a decrease of the intensity band at 1665 cm^{-1}, 3265 and 3100 cm^{-1}. Two different IR bands have proposed as internal standard depending on the range of acetyl contents. The first used for the degree of acetylation and the second band used as a reference, the acetyl content is defined as the absorbance ratio of $\frac{A_{1665}/A_{3450}}{1.33} \times 100$ (Kubita et al., 1989). Deacetylation and regeneration process disrupting the initial crystal lattice of the parent chitin, this can be observed for the broadening band at 3450 cm^{-1} $[(OH)_5 \cdots B(5)]$ and the frequency shift of OH stretching. The shift can be used as a measure of the intermolecular hydrogen bonding. The ratio of the intensity at 1379 and 2920 cm^{-1} for chitin was suggested as an index of crystallinity. The previous bands are found in chitin and treated chitin with different intensities.

From Table 1 it is clear that, the two relative absorbance bands (3266/1325 cm^{-1}) and (310/1325 cm^{-1}) decrease by treating chitin. This can be attributed to the lower acetyl content in case of treated chitin. This means that during treatment of chitin with acid, alkali and hypochlorite solution some exhaustion of amide groups become took place. The relative absorbance of either link band at 1120 cm^{-1} is slightly decreases by treatment. Also, from Table 1 it was noticed that the crystallinity indices of chitin is higher than that of treated chitin This is in good agreement with the decrease in the absorbance of the either link, and this is may due to the hydrolysis of some acetamide group.

Table 1
The different variations of chitin and its treated one

Materials	Crystallinity index (CrI)	Acetyl acetate (%)	Amide group (3266/1325)	Amide group (3100/1325)
Chitin	1.925	90.8	1.136	0.936
Chitin acid	1.278	83.2	1.130	0.863
Chitin base	1.329	87.9	1.013	0.837
Chitin hypochlorite	1.295	85.8	1.106	0.908

The dielectric constant (ε') of chitin and treated chitin by acid, base and hypochlorite were measured in the frequency range (0.1 kHz–3 MHz) as shown in Fig. 2 and its inset. From this figure it is clear that, the dielectric constant (ε') was decreased with increasing frequency. This is due to the dielectric dispersion as a result of the Lag of the molecules behind the alternation of the electric field which was observed when frequency is less than 10 kHz. After frequency up to 10 kHz, in the presence of an externally applied electric field the molecules tend to orient themselves in the direction of the field and the effect of frequency on the (ε') attributed to small (Von Hippel, 1995; McHale, 1999; Clausius, 1979; Tareev, 1965). Generally, the polarizability (α) increases by increasing the dipolar moment, orientation and reorientation motion which is due to the decrease of (ε') at lower frequency. The slight decrease of (ε') after 10 kHz may be due to the effect of the polymer main chain dynamics, such that molecules bound to the hydrophilic groups of the anhydroglucose (AGU) resulting in decrease of the dipolar moment of the side groups (Einfeldt, Meibner, & Kwasniewski, 2001). In chitin we suggest a site model of the repeating unit, the anhydroglucose amine unit, all relevant dipolar moments and all possible reorientation motions were labeled. The types of dipolar and movable sites are; 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 C–O linkage, also the C_7 position has one mobility

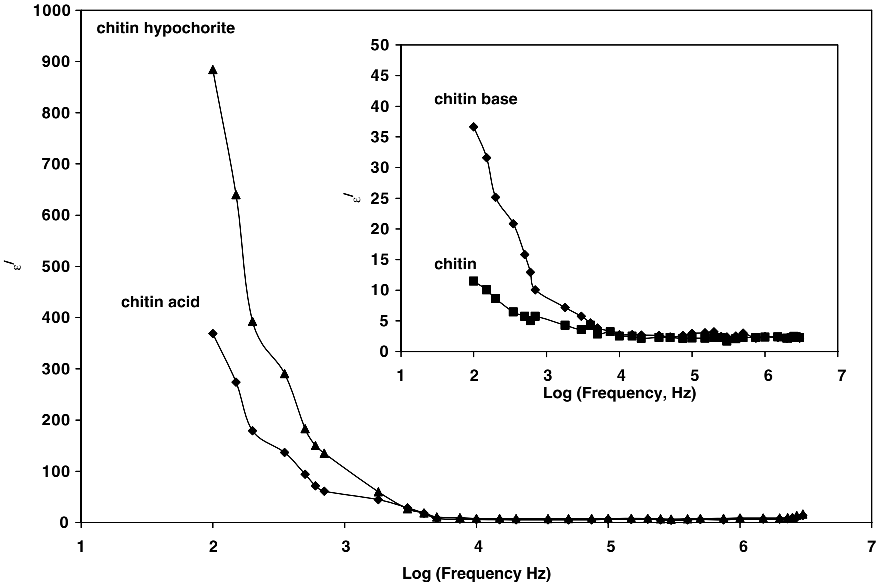
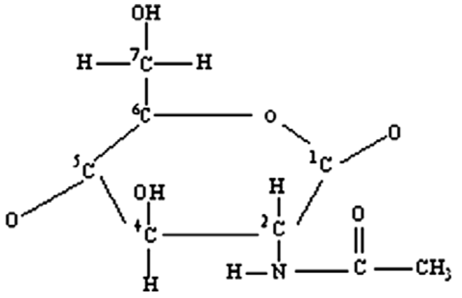


Fig. 2. Variation of real part of dielectric constant (ε′) with log frequency for chitin acid, base and hypochlorite at $T = 30$ °C.

around C_6–C_7 and an additional rotation mobility around the C_7–O linkage in the structure (1) (Einfeldt et al., 2001).



On the other hand, the dependence of (ε′) on the frequency was adequately interpreted in terms of an equivalent circuit model Goswami and Goswami (1973). According to this model the measured series capacitance C_s which depends directly on (ε′) [$\varepsilon' = \text{constant} * C_s$] is given by $C_s = C' + \frac{1}{\omega^2 R^2 C'}$. This relation predicted that C_s should be decreasing with increasing frequency (ω), eventually, tending to a constant value C_s for any given frequency and this effect was clearly observed in Fig. 2 for all samples under investigation.

By comparing (ε′) of chitin and its treated one in Fig. 2 and inset we noticed that, the dielectric constant (ε′) of chitin hypochlorite is higher than that of acid and base treated chitin up to 10 kHz. This can be attributed to strengthening of the intermolecular interaction by hydrogen bonding. The rigidity of the structure formed by intermolecular interaction hydrogen bond will decrease the mobility of molecules and this leading to increase of (ε′). This is in agreement with IR data which indicates that the acetyl content of chitin hypochlorite was higher than the other samples.

The variation of the dielectric loss (ε″) for chitin and treated chitin with frequencies was shown in Fig. 3 and inset. From this figure it was found that, (ε″) decrease with increasing frequency due to the increase of the polarizability (α) by increasing the dipolar moment, orientation and reorientation motion and its lead to the decrease of (ε″) at lower frequency; the same behavior was observed in (ε′). The main contribution to dielectric relaxation arises, in the frequency range used, from the motion of polar side groups only and no contribution from the ring and the backbone of the main chain. One type of β-relaxation was observed at frequency about 2.5 kHz in chitin and treated chitin which is due to the rotation of polar side groups. The relaxation process is expected and it is strength vary with the number of dipolar groups per unit chain length. Also, it varies with the number of crosslink, chain entanglement in the amorphous phase, number and size of the crystallites in it. Treated process accompanied by introducing polymer chain compacted between chitin chains and few of them were event at the surface of rigid structure. By comparing the intensity of relaxation peaks it was found that it increases with increasing polymer parent. In the case of chitin hypochlorite the rigidity of the structure due to intermolecular hydrogen bonding will reduce the mobility of sided groups which increase the dielectric loss. Thus the dielectric magnitude of relaxation will be increased, reaching maximum at chitin hypochlorite.

The dependence of AC electrical conductivity on the frequency for chitin and treated chitin was shown in Fig. 4. From this figure it was found that, two different regions were observed. In the first region, the conductivity was nearly constant with increasing frequencies up to 50 kHz. This behavior is acceptable because the AC field is not sufficient to activate the charge carriers and increases their mobilities giving a nearly constant of conductivity up to 50 kHz. The deviation from the linearity in the high

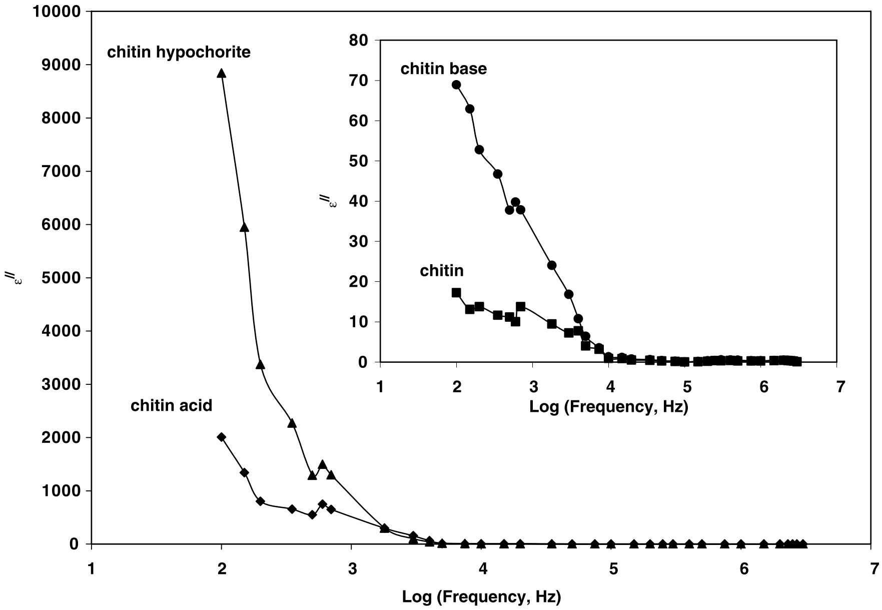


Fig. 3. Variation of imaginary part of dielectric constant (ε″) with log frequency for chitin acid, base and hypochlorite at $T = 30$ °C.

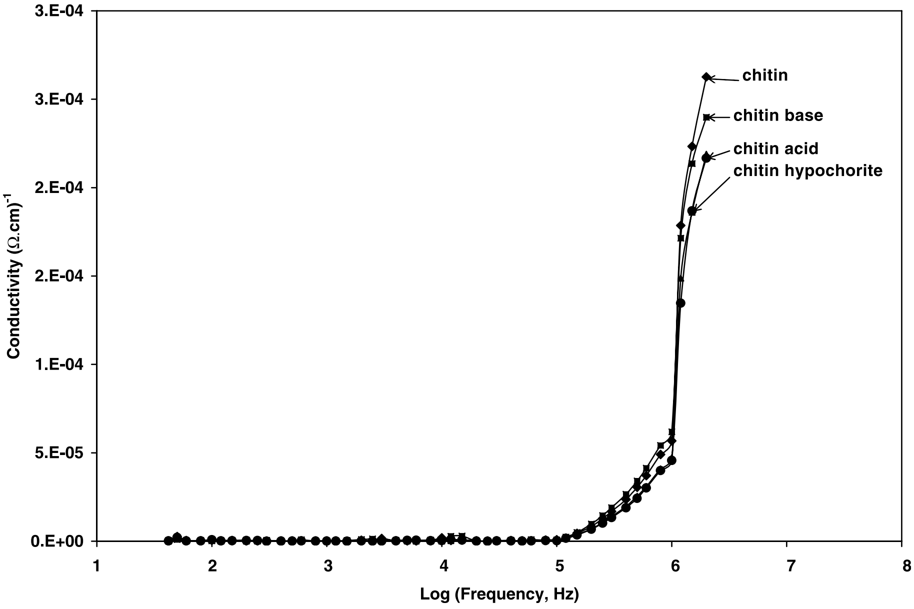


Fig. 4. Variation of AC electrical conductivity with log frequency for chitin acid, base and hypochlorite at $T = 30$ °C.

frequencies may be due to the dispersion of molecules. Generally, the electrical conductivity of the polymer depends on the presence of free ions connected chemically with macromolecule. The molecular chain does not participate in the transfer of electrical charge (Fancher, Graham, Kulaske, Santee, & Walter, 1966). Hydrogen bonded polymer usually have higher conductivity with respect to non-hydrogen bonded polymers. When crystallinity decreases the mobility and conduction decrease consequently. The tunneling model is applied in the mechanism of charge carriers at higher frequency 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 non-occupied state of a neighboring molecule with energy conserved in the tunneling process (Clarke, Ray, Tsibouklis, & Werninck, 1991). The energy depends on the spin and therefore, the electron in the excited state may tunnel to its neighboring 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 increases with increasing frequency (Elliott, 1987). The available experimental results on the frequency dependence of AC conductivity have revealed a considerable similarity of behavior for all samples. An empirical relation can express the higher frequency dependence of AC conductivity as follows, $\sigma_{AC} \propto (2\pi f)^n$ where n is not a constant for all substances (Saleh, Gould, & Hassan, 1993).

4. Conclusion

The change of the molecular structure which studied for chitin and treated chitin by acid, base and hypochlorite revealed that the crystallinity index of chitin is higher than that of treated chitin due to the decrease of methyl or amine groups. The decrease of dielectric constant (ε') with frequencies (less than 10 kHz) was interpreted interms of the dispersion process. The β-relaxation was observed at (2.5 kHz) in the dielectric loss (ε''). The hopping conduction mechanism was applied for the conductivity at higher frequency. The data of the dielectric constant enhances the change of the vibrational modes.

References

Austin, P. R. (1977). US patent, 4, 05745–05747.

Bassler, H. (1984). *Philosophical Magazine B, 50*, 347.

Burchard, W. (1983). *Advances in Polymer Science*, 48.

Clarke, P. J., Ray, A. K., Tsibouklis, J., & Werninck, A. R. (1991). *Journal of Materials Science and Materials in Electronics, 2*, 18.

Clausius, R. (1979). *Mechanische Warmetheorie, 2*, 94.

Duarte, M. L., Ferreira, M. C., Marvao, M. R., & Rocha, J. (2002). *International Journal of Biological Macromolecules, 31*(1–3), 1.

Einfeldt, J., Meibner, D., & Kwasniewski, A. (2001). *Progress in Polymer Science, 26*, 1419.

Einfeldt, J., Meibner, D., & Kwasniewski, A. (2003). *Journal of Non-Crystalline Solids, 320*, 40.

Elliott, S. R. (1987). *Advances in Physics, 36*(2), 135.

Fancher, J. A., Graham, J. D., Kulaske, J. V., Santee, E. R., & Walter, E. R. (1966). *Journal of Physical Chemistry, 70*, 3738.

Franz, G. (1991). *Polyscaccharide*. Berlin: Springer.

Gilbert, R. D. (1993). *International Fiber Science and Technology, 12*, 357.

Goswami, A., & Goswami, A. P. (1973). *Thin Solid Films, 16*, 175.

Havriliak, S., Jr., & Havriliak, S. (1996). *Journal of Polymers, 37*, 4107.

Kubita, K., Koyama, Y., Nishamura, S., & Kamiya, M. (1989). *Chemical Society of Japan*, 1597–1598.

Lindsey, C. P., & Patterson, G. D. (1980). *Journal of Chemical Physics, 73*, 3348.

McHale, Jeanne L. (1999). *Molecular spectroscopy*. Prentice-Hall, Inc.

Mehendru, P. C., Pathak, K., Jain, K., & Mehendru, P. (1997). *Physica Status Solidi A, 42*, 403.

Mink, R., & Blackwell, J. (1978). *Journal of Molecular Biology, 120*, 1167.

Muzzarelli, R. A. A. (1973). *Natural chelating polymers*. New York: Pergamon Press, pp. 83–227.

Muzzarelli, R. A. A. (1986). In R. A. A. Muzzarelli, C. Jeuniaux, & G. W. Gooday (Eds.), *Chitin in nature and technology* (pp. 337–351). New York: Plenum Press.

Pangburn, S. H., Trescony, P. V., & Heller, J. (1988). In J. P. Zikakis (Ed.). *Chitin, Chitosan and related enzymes* (pp. 1–19). London: Academic Press.

Pariser, E. R., & Lombordi, D. P. (1980). *Chitin Source Book: A Guide to Research Literature*. New York: John Wiley & Sons.

Rathke, T. D., & Hudson, S. M. (1994). *Journal of Material Science, 34*, 375.

Ravi Kumar, M. N. V. (1999). Chitin and chitosan fibres: a review. *Bulletin of Material Science, 22*, 905.

Ravi Kumar, M. N. V. (2000). Chitin and chitosan fibres: an overview on chitin and chitosan applications. *Reactive and Functional Polymers, 46*.

Ravi Kumar, M. N. V., Rajakala Sridhari, T., Durga Bhavani, K., & Dutta, Pradip Kumar (1998). Trends in Colour Removal from Textile mill Effluents. *Colourage*, 25.

Roling, B. (1999). *Journal of Non-Crystalline Solids, 244*, 34.

Rudall, K. M. (1963). *Advances in Insect Physiology, 1*, 257.

Saleh, A. M., Gould, R. D., & Hassan, A. K. (1993). *Physica Status Solidi A, 139*, 379.

Shinka, H. C., Talmar, I. M., & Srivastava, A. P. (1989). *Thin Solid Films, 82*, 229.

Sullivan, D. E., & Deutsch, J. M. (1975). *Journal of Chemical Physics, 62*, 2130.

Tareev, B. (1965). *Materials for electrical engineering*. Moscow: Higher School Publishing House.

Von Hippel, Arthur (1995). *Dielectric materials and applications*. Boston, London: Artech House.

Yalpani, M., Johnson, F., & Robinson, L. E. (1992). *Chitin and chitosan: sources, chemistry, biochemistry, physical properties and applications*. Amsterdam: Elsevier.

Zhang, M., Haga, A., Sekiguchi, H., & Hirans, S. (2000). *International Journal of Biological macromolecules, 27*, 99.