Existance of Intermolecular relaxation and Stokes-Einstein-Debye relation in supercooled D-arabinose

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Abstract— Broadband dielectric spectroscopy has been used to study the different relaxation behavior in the supercooled state of D-arabinose over a wide frequency ($10^{-3} – 10^7$ Hz) and temperature range (120-360 K). In addition to the main relaxation process (α) which is responsible for the glass transition phenomena, two more relaxation processes viz. β- & γ- were also observed below the glass transition temperature. The slower secondary relaxation or β-process has been identified as true intermolecular relaxation and faster one (γ-process) is probably the rotation of hydroxymethyl ($-CH_2OH$) side group attached to the sugar ring. The temperature dependence of various dielectric parameters viz. τ_α, τ_β, τ_γ and τ_σ have been critically examined. The current experimental result shows that, $\log_{10} \sigma_{dc}$ vs. $\log_{10} \tau_\alpha$ dependence is nonlinear and hence can be described with the fractional Stokes-Einstein-Debye relation.

Index Terms—*Dielectric relaxation, glass transition, intermolecular relaxation, Stokes-Einstein-Debye relation.*

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1 INTRODUCTION

THE molecular origin of the secondary relaxation and its possible connection to the primary or structural relaxation is the two important aspects concerning the relaxation dynamics of glass forming materials. It is well accepted that some secondary relaxations have an intra-molecular origin which originates from the motion of side groups of the molecules almost decouple from the rest part. Besides, in some other molecular systems, the observed secondary relaxation reflects the motion of the entire molecule i. e. of intermolecular in nature. The secondary processes caused by this mechanism are usually known as Johari-Goldstein (or JG-) [1], [2] relaxation processes which is considered to reflect a universal relaxation mechanism of glass forming materials.

Due to the increasing importance of intermolecular relaxation (or JG-) in glass forming materials, a lot of work has been carried out to identify the JG-relaxation in glass forming materials such as polymers [3], carbohydrates [4], [5], [6], [7], [8], [9] as well as orientationally disordered crystals [10], [11]. Among these glass forming materials, carbohydrates (mono-, di-, and polysaccharides) have been studied extensively both in anhydrous form [4], [5], [6], [7], [8], [9] as well as aqueous solutions [9], [12], [13]. Because of the presence of the strongly polar OH groups and, hence, hydrogen (H–) bonding in carbohydrates, the dielectric relaxation spectroscopy has been extensively used to understand the presence of various relaxation processes. Earlier broadband dielectric relaxation studies [4], [5], [6], [7], [8] on various carbohydrates (mono-, di-, and polysaccharides) have identified the presence of JG-relaxation. These dielectric studies on aldopentoses viz. D-ribose, 2-deoxyribose and D-arabinose had predicted the existence of JG-relaxation, but the temperature dependence of relaxation times of this process is still missing. In order to find the relaxation time of

JG-relaxation and other dielectric parameters such as the relation between dc electrical conductivity and dielectric relaxation time, we have remeasured the dielectric spectra of D-arabinose in a broad temperature range. Here, we present the results of our measurements of broadband dielectric spectroscopy studies on this material (D-arabinose) over a wide range of temperatures.

2 EXPERIMENTAL

The material D-arabinose ($M_W \sim 150.13$ g/mol) obtained from Sigma Aldrich (purity ≥ 99 %) and used as received. To prepare the sample, the crystalline D-arabinose has been placed on 30 mm gold plated electrodes. The crystals were melted directly over them by keeping the temperature around their melting temperatures, up to turn the samples transparent and care was taken to prevent thermal degradation. Then other electrode of 20 mm diameter has been put over 30 mm diameter electrode with 0.1 mm Teflon spacers. Now the samples were quenched putting them in liquid nitrogen to prevent crystallization during cooling.

Novocontrol alpha analyzer, a broadband dielectric spectrometer has been used to measure the complex dielectric function [$\varepsilon^*(\omega) = \varepsilon'(\omega) – i \varepsilon''(\omega)$, where $\omega = 2\pi f$], in the frequency (*f*) range 1 mHz – 10 MHz. After cooling at a rate of 10 K/min, isothermal frequency scans recording were performed during heating from T = 120 to 280 K with steps of 5 K and from T = 280 to 350 K with steps of 2.5 K. The sample temperature was controlled with stability better than ± 0.1 K.

In order to analyze the results, the following frequency domain expression has been used to fit the dielectric spectra, which is based upon the asymmetric Havriliak-Negami (HN) function [14]. Following common practice in all cases, the entire loss spectrum is fit by the sum of three processes plus dc-conductivity:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{\left[1 + \left(i\omega\tau_j\right)^{\alpha_j}\right]^{\gamma_j}} + \frac{\sigma_0}{i\omega\varepsilon_0} \quad (1)$$

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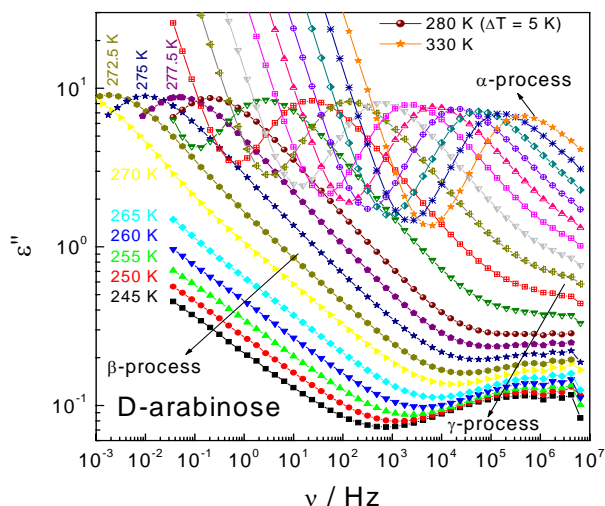
Fig. 1. Dielectric loss spectra of D-arabinose for temperatures between 330 K and 245 K as indicated.

Here, $\Delta\varepsilon_j = \varepsilon_{sj} - \varepsilon_{\infty j}$ is the relaxation strength of the jth process, τ_j is the HN- relaxation time, α_j and γ_j represent the symmetric and asymmetric broadening of the loss curve ($0 < \alpha, \alpha\gamma \leq 1$), and ε_∞ is the high frequency limit of the real part of the permittivity. One particular case of the above HN expression is the symmetric Cole-Cole (CC) function which is obtained by setting $\gamma = 1$. In the present case, an HN-function was used to fit α-process, γ - process and a Cole-Cole function to fit β-process.

3 RESULTS AND DISCUSSION

Arabinose is an aldopentose monosaccharide containing five carbon atoms, including an aldehyde (-CHO) functional group. It exists in nature in two forms namely D- and L-form. However, L-arabinose is in fact more common than D-arabinose in nature and is found in nature as a component of biopolymers such as hemicellulose and pectin. L-form has been studied by earlier researchers [15] using dielectric spectroscopy and differential scanning calorimetry. They found, only one secondary relaxation process in addition to the primary relaxation process. Fourteen years later Kaminski and co-workers [5] studied both forms and their equimolar mixture using broadband dielectric spectroscopy, but surprisingly they also reported only one secondary relaxation process. Probably they could not resolve another secondary relaxation process which emerges from the excess wing on the high frequency side of the primary relaxation process. In the present task, we have critically examined the data and succeeded to resolve another secondary relaxation process (designated as β-process), emerges from the excess wing on the high frequency side of the primary relaxation process. Depicted in Figure 1, is the frequency dependent of imaginary part of permittivity (ε") of D-arabinose at various temperatures. The dielectric loss spectra of pure D-arabinose reveal two clearly resolved relaxation process contributed by the primary relaxation (α-process) and a secondary relaxation called γ-process. However, as we go towards lower temperature i. e. below the glass transition

temperature (T_g), a shoulder can be seen in the loss spectra in between the primary-loss peak (α-) and secondary loss peak (γ-process). This new feature indicates the presence of another secondary relaxation process (designated as β-process in Figure 1) located at frequencies intermediate between the primary relaxation (α-) and the clearly resolved γ- relaxation process. Hence in addition to the primary relaxation process (α-), two resolved secondary relaxation processes (designated as β- and γ-) at a temperature lower than T_g can be seen in supercooled D-arabinose. The γ-process is clearly visible in the vicinity of glass transition temperature (T_g) and becomes more pronounced in the glassy state. It is worth to mention that the γ-process becomes asymmetric in the glassy state. Therefore we have applied the Havriliak-Negami (HN) function (eq. 1) to the best fit of γ-process. However the β-process is well described by Cole-Cole function in the whole temperature range. The same behavior of γ-process was also reported recently by Singh et al. [8] for D-lyxose and earlier by Kaminski et al. [4], [5], [6], [7] for other sugars. Some representative examples of the fitting procedure are shown in Figure 2 at three fixed temperatures to show the behavior of α-process, γ-process and the existence of β-process. Clearly the α-process was well described by HN-function (eq. 1) with large α_{HN} and γ_{HN} values. According to our fitting results, α_{HN} ranges from 0.68 to 0.80 and γ_{HN} ranges from 0.39 to 0.62 which is a typical value of fragile glass forming materials. Almost similar behavior was also observed by earlier researchers in D-arabinose [5], [12], [15] and D-lyxose [8].
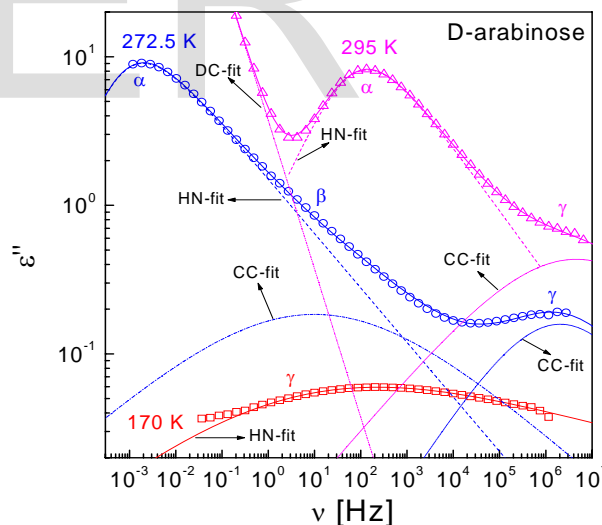

Fig. 2. The dielectric loss spectra at T = 170, 270.5, and 295 K to show the existence of various relaxation processes. The dashed lines correspond to the HN-fit for the α-processes, dashed dotted line corresponds to the CC-function for the resolved β-process and dashed double dotted line corresponds to the DC-fit for conductivity. Solid lines represent the typical ansatz fit. The corresponding parameters are: T = 170 K (α_{HN} = 0.24, γ_{HN} = 0.36, $\Delta\varepsilon$ = 0.96, $\log_{10}\tau_{HN}$ = -1.31); T = 272.5 K (α-process: α_{HN} = 0.76, γ_{HN} = 0.48, $\Delta\varepsilon$ = 36.8, $\log_{10}\tau_{HN}$ = 2.27; β-process: α_{HN} = 0.27, γ_{HN} = 1, $\Delta\varepsilon$ = 1.69 $\log_{10}\tau_{HN}$ = -1. 80; γ-process: α_{HN} = 0.48, γ_{HN} =1, $\Delta\varepsilon$ = 0.80, $\log_{10}\tau_{HN}$ = -7.1); T = 295 K (α-process: α_{HN} = 0.70, γ_{HN} = 0.61, $\Delta\varepsilon$ = 33.54, $\log_{10}\tau_{HN}$ = -2.67; γ-process: α_{HN} = 0.37, γ_{HN} = 1, $\Delta\varepsilon$ = 2.92, $\log_{10}\tau_{HN}$ = -7.45).

Depicted in Figure 3, is the temperature dependence of dielectric relaxation times of different relaxation processes observed in pure D-arabinose. The temperature dependence of relaxation times of α-process (τ_α) as well as the conductivity relaxation process ($\tau_\sigma = \varepsilon_0\varepsilon_s/\sigma_{dc}$) was described by Vogel-Fulcher-Tammann (VFT) equation [16], [17] given by,

$$\log_{10}\left[\tau(T)/s\right] = A + \frac{B}{T - T_0} \qquad (2)$$

where T_0 is the temperature at which the dynamics of the system tend to diverge, A is a logarithmic pre- exponential factor and B is a constant. On the other hand, the temperature dependence of relaxation times of both secondary relaxation processes (β- & γ-) were described by Arrhenious equation (put $T_0 = 0$ in eq. 2). The best VFT-fit parameters in the order A, B and T_0 for processes σ_{DC}-, α-, β- & γ- are as follows. σ_{dc}-process: -10.50, 1426.28 K, 182.97 K; α-process: -14.84, 1039.61 K, 211.25 K; β-process: -18.42, 4567.45 K, 0; γ-process: -14.74, 1966.88 K, 0. Based on the criterion of dielectric glass transition temperature (T_{gD}) where the relaxation time reaches upto a value of 100 sec, the present VFT-fit of α-process imply glass transition temperature $T_{gD} = 272.9$ K. This value is consistent with the calorimetric glass transition temperature of D-arabinose reported by by Singh et al. [12]. Thus we may conclude that the primary relaxation or α-process is related to the glass transition phenomenon in D-arabinose. Moreover the VFT-fit has also been used to calculate fragility index [18], which is defined as:

$$m = \frac{d\left(\log_{10}\tau_\alpha\right)}{d\left(T_g/T\right)}\Bigg|_{T=T_g} \qquad (3)$$

The value of 'm' obtained from above equation comes out to be 74.5, which is consistent with the fragility index obtained by earlier researchers in pure D-arabinose [5], [11]. However this value is slightly higher than the fragility index of their isomers viz. D-lyxose [8] and D-ribose [4].

Now focusing on results of resolved secondary relaxation or β-process, the relaxation time of this process has been determined using cole-cole fit function. The activation energy of this process is about 4567.45 K or 87.4 ± 5 kJ/mol. This value is very close to the activation energy of β-process found in other isomer D-lyxose [8]. Based on high pressure sensitivity of this process, Singh et al. [8] concluded that this process is of intermolecular or JG-type in nature. Also the observed activation energy of β-process in the present case is within the range (73-98 kJ/mol) of the activation energies of JG-process found in mono- di- and polysaccharides [6], [7], [8]. These results imply that the observed β-process in D-arabinose has the same origin as in the case of D-lyxose [8] and other saccharides [6], [7] i.e. of intermolecular or JG-relaxation process.

Further throwing more light on the results of another secondary relaxation or γ-process observed in D-arabinose. The calculated activation energy of this process is about 1966.88 K or 37.5 kJ/mol. This result is consistent with the order of magnitude of the activation energy reported by Singh et al. [11] as well as by Kaminski et al. [5] in glassy D-arabinose. Other
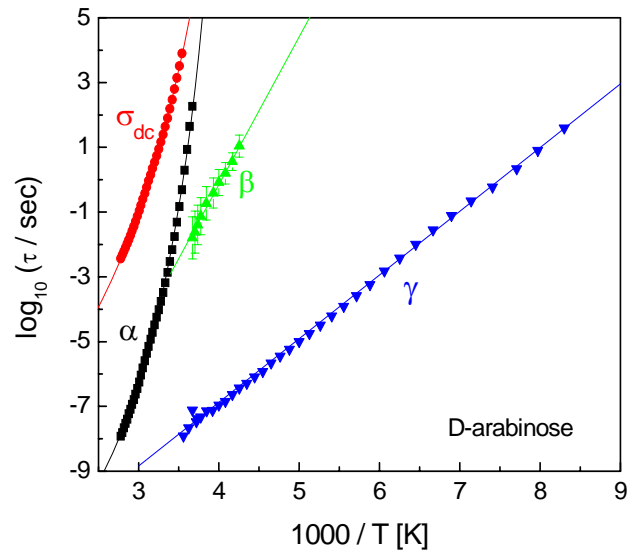
Fig. 3. Temperature dependence of the dielectric relaxation times of different relaxation processes for D-arabinose. In the order from slow to fast process, the time constants are for dc-conductivity (τ_σ), the primary structural process (τ_α), the resolved secondary relaxation (τ_β) and the secondary relaxation (τ_γ). The lines along the τ_σ and τ_α symbols are VFT fits, the lines near the τ_β and τ_γ data represent an Arrhenius fits.
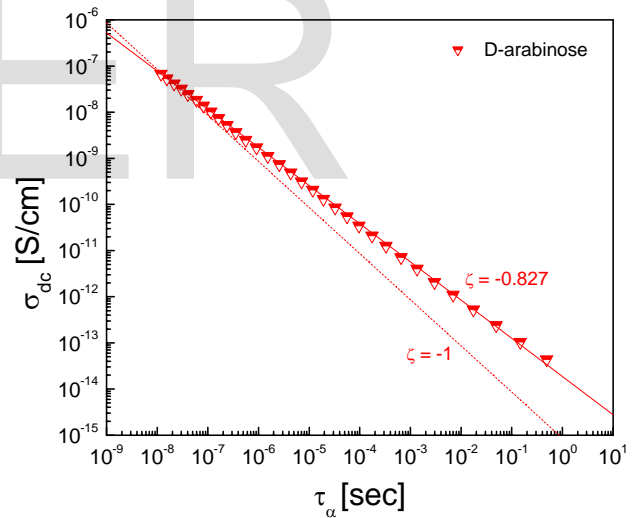
Fig. 4. Log-log plot of dc conductivity (σ_{dc}) verses structural relaxation time (τ_α) for supercooled D-arabinose. A straight line (dashed line) of slope -1 is also drawn for caoparision. The solid line along symbols is the fit to fractional-Stokes-Einstein-Debye relation (eq. 4).

monosaccharides viz. D-lyxose [8], D-ribose [4] also show the same relaxation behavior and approximately same activation energy. The same relaxation process also exists in disaccharides as well as polysaccharides [7], [9]. They identify this relaxation as originating from local chain motion. Gangasharan and Murthy [15] identified the origin of this process as the segmental rotation of a linear chain of the monosaccharides unit. While Noel et al. [9] have suggested that this process may be linked to the rotation of hydroxymethyl groups at-

tached to the sugar ring. Recently Singh et al. [8] have identified the origin of γ-process of D-lyxose as the rotation of hydroxymethyl (CH_2OH) side group attached to the sugar ring. Since D-arabinose is an isomer of D-lyxose and both belong to Aldopentoses family and also this process is insensitive to pressure, thus we may conclude that the γ-relaxation in D-arabinose has the same origin as those of γ-process observed in D-lyxose i.e. due to the rotation of the CH_2OH group (intramolecular origin).

It is very well known that dielectric spectroscopy provides simultaneous measurements of primary relaxation time $τ_α$ (rotational dynamic component) and dc conductivity (translational component) in the presence of electric field over a broad dynamic range. When these two quantities are coupled, a relationship exists between the temperature dependence of the α-relaxation time and the dc conductivity of the liquid as $σ_{dc}(T) τ_α(T)$ = constant, usually known as Stokes-Einstein-Debye relation. However, the breakdown of Stokes-Einstein-Debye relationship is oftenly observed in glass forming materials near the glass transition temperature [3], [19], [20]. So fractional-Stokes-Einstein-Debye equation is required to describe the experimental data:

$$σ_{dc}(T) \, τ_α(T)^ζ \cong const \qquad (4)$$

Where $ζ$ is the fractional exponent ($0 < ζ ≤ 1$). In order to test this relation, a log-log plot of $σ_{dc}$ against $τ_α$ for D-arabinose is shown in Figure 4. A dashed line of slope -1 is also shown in the figure. On closer inspection of this Figure 4, one can notice that eq. 4 well describes the data with an exponent $ζ = -0.827 ± 0.02$. This exponent value is consistent with commonly reported values in the range from 0.75 to 0.91 [3], [19], [20]. Therefore we may conclude that for D-arabinose, there is an enhancement of translational ionic motion in comparison with the orientational molecular motions on approaching the glass transition temperature (T_g).

3 CONCLUSION

Dielectric relaxation behavior of supercooled D-arabinose has been examined using broadband dielectric spectroscopy. We have succeeded to resolve the secondary relaxation process (β-process) and determined the temperature dependence of relaxation time of this process. The activation energy for this process was found to be 86.3 ± 5 kJ/mol and has been identified as true intermolecular relaxation or JG-process. The other secondary process viz γ-process has also been observed having almost the same activation energy as observed by earlier researchers. Additionally, a breakdown of the Stokes-Einstein-Debye relation ($\log_{10} σ_{dc}$ vs. $\log_{10} τ_α$) was observed revealing an enhancement of translational ionic motions in camparison with the orientational molecular motion as the glass transition temperature is approached.

ACKNOWLEDGMENT

REFERENCES

[1] G. P. Johari and M. Goldstein, "Viscous liquids and the glass transition. II. Secondary relaxations in glasses of of rigid molecules," *J. Chem. Phys.* Vol. 53, pp. 2372-2388, 1970.

[2] G. P. Johari and M. Goldstein, "Viscous liquids and the glass transition. III. Secondary relaxations in aliphatic alcohols and other non rigid molecules," *J. Chem. Phys.* Vol. 55, pp. 4245-4252, 1971.

[3] C. M. Roland, S. Hansel-Bielowka, M. Paluch and R. Casalini, "Super-cooled dynamics of glass forming liquids and polymers under hydrostatic pressure," *Rep. Prog. Phycs.* Vol. 68, pp. 1405-1478, 2005.

[4] K. Kaminski, E. Kaminska, P. Wlodarczyk, M. Paluch, J. Ziolo and K. L. Ngai, "Dielectric relaxation study of the dynamics of monosaccharides: D-ribose and 2-deoxy-D-ribose" *J. Phys. : Condens. Matter* Vol. 20, pp. 335104, 2008.

[5] K. Kaminski, E. Kaminska, S. Pawlus, P. Wlodarczyk, M. Paluch, J. Ziolo, A. Kasprzycka, W. Szeja, K. L. Ngai and J. Pilch, "Dielectric properties of two diastereoisomers of the arabinose and their equimoler mixture," *Carbohydr. Res.* Vol. 344, pp. 2547-2553, 2009.

[6] K. Kaminski, E. Kaminska, M. Paluch, J. Ziolo and K. L. Ngai, "The true Johari-Goldstein β-relaxation of monosaccharides," *J. Phys. Chem. B.* Vol. 110, pp. 25045-25049, 2006.

[7] K. Kaminski, E. Kaminska, S. Hensel-Bielowka, E. Chelmecka, M. Paluch, J. Ziolo, P. Wlodarczyk and K. L. Ngai, "Identification of the molecular motions responsible for the slower secondary β-relaxation in sucrose," *J. Phys. Chem. B.* Vol. 112, pp. 7662-7668, 2008.

[8] L. P. Singh, A. Alegria and J. Colmenero, "Broadband dielectric spectroscopy and calorimetric investigations of D-lyxose" *Carbohydr. Res.* Vol. 346, pp. 2165-2172, 2011.

[9] T. R. Noel, R. Parker and S. G. Ring, "A comparative study of the dielectric relaxation behavior of glucose, maltose and their mixtures with water in the liquid and glassy states," *Carbohydr. Res.* Vol. 282, pp. 193-206, 1996.

[10] L. P. Singh and S. S. N. Murthy, "Study of secondary relaxation in disordered plastic crystals of isocyanocyclohexane, cyanocyclohexane and 1-cyanoadamantane," *J. Chem. Phys.* Vol. 129, pp. 094501, 2008.

[11] L. P. Singh and S. S. N. Murthy, "Dielectric and calorimetric investigation of an unusual two-component plastic crystal: cyclohexanol-neopentylglycol," *Phys. Chem. Chem. Phys.* Vol. 11, pp. 5110-5118, 2009.

[12] L. P. Singh, S. Cerveny, A. Alegria and J. Colmenero, "Broadband dielectric spectroscopic, Calorimetric and FTIR-ATR investigations of D-arabinose aqueous solutions" *Chem Phys Chem.* Vol. 12, pp. 3624 - 3633, 2011.

[13] N. Shinyashiki, M. Shinohara, Y. Iwata, T. Goto, M. Oyama, S. Suzuki, W. Yamamoto, S. Yagihara, T. Inoue, S. Oyaizu, S. Yamamoto, K. L. Ngai and S. Capaccioli, "The glass transition and dielectric secondary relaxation of fructose-water mixture" *J. Phys. Chem. B,* Vol. 112, pp. 15470 – 15477, 2008.

[14] S. Havriliak and S. Negami, "A complex plane representation of dielectric and mechanical relaxation processes in some polymers," *Polymer*, Vol. 8, pp. 161-210, 1967.

[15] Gangasharan and S. S. N. Murthy, ''Nature of the relaxation processes in the supercooled liquid and glassy states of some carbohydrates,'' *J. Phys. Chem.* Vol. 99, pp. 12349-12354, 1995.

[16] J. Wong and C. A. Angell, ''Glass structures by spectoscopy'' Marcel Dekker, New York, 1976.

[17] G. S. Fulcher, ''Analysis of recent measurements of viscosity of glasses'' *J. Am. Ceram. Soc.,* vol. 8, pp. 339-355, 1925.

[18] C. A. Angell, "Relaxation in liquids, Polymers and plastic crystals:

Strong/fragile patterns and problems," *J. Non-Cryst. Solids*, Vol. 131-133, pp. 13-31, 1991.

[19] S. Corezzi, E. Campani, P. A. Rolla, D. Fioretto, "Changes in the dynamics of supercooled systems revealed by dielectric spectroscopy," *J. Chem. Phys.* Vol. 111, pp. 9343-9351, 1999.

[20] G. P. Johari and O. Andersson, ''On the non-linear variation of dc conductivity with dielectric relaxation time,'' *J. Chem. Phys.* Vol. 125, pp. 124501, 2006.

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