

Broadband Dielectric Spectroscopy and Electric Modulus Analysis of Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and Related Copolymers Films

**T. Fahmy^{1,2}, M. T. Ahmed², A. El-kotp^{1,2},
H. G. Abdelwahed^{1,3} and M. Y. Alshaer¹**

*¹Plasma Technology and Material Science Unit (PTMSU),
Physics Department, College of Science and Humanitarian Studies,
Prince Sattam bin Abdulaziz University, Alkharj, KSA.*

*²Polymer Research group, Physics Department, Faculty of Science,
Mansoura University, 35516 Mansoura, Egypt.*

*³Theoretical Research group, Physics Department, Faculty of Science,
Mansoura University, 35516 Mansoura, Egypt.*

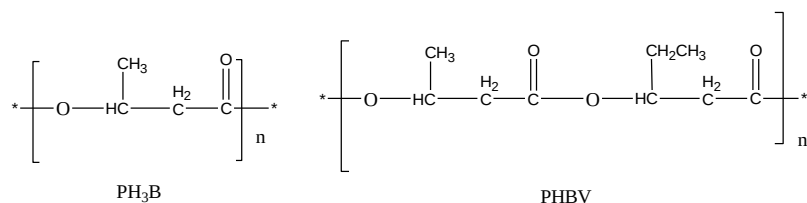
Abstract

The dielectric relaxation behavior of pure (3-hydroxybutyrate), PHB and its copolymer (3-hydroxybutyrate-co-3-hydroxyvalerate), PHB-HV, is investigated in wide range of frequency from 0.001 Hz to 1×10^7 Hz at different fixed temperatures. It is observed that, pure PHB and its copolymers with different ratios of hydroxyvalerate are characterized by high dielectric constant at low frequency and high temperature. This behavior is attributed to interfacial polarization, (Maxwell-Wagner-Sillars) polarization. The behavior of imaginary part of electric modulus (M'') with temperature for the samples is characterized by two different relaxational peaks. The first one is positioned in the region of T_g of pure PHB, whereas, the second peak at temperature ~ 338 °K, and is assigned as Maxwell-Wagner-Sillars (MWS) relaxation. AC conductivity of all samples is investigated. The Arrhenius plots of AC conductivity showed a remarkable change in the conduction mechanism in glass transition temperature region of pure PHB.

Keywords: Broadband, Dielectric Relaxation, Pure (3-hydroxybutyrate), Interfacial Polarization, Electric Modulus

Introduction

Poly (hydroxyalkanoates) are biological polyesters produced by microorganisms [1,2]. The chemical structure of pure PHB and its copolymer is shown as follow:



Poly (hydroxyl butyrate) is considered as crystalline polyester and has great technological applications, such as, disposable items and biomedical applications, because of its biocompatibility. The physical properties of poly (hydroxyalkanoates) can be modified by adopting the monomer ratio of PHA. PHAs are biodegradable and biosynthetic polymers in comparison with other biodegradable plastics [3]. The applications of PHB are limited because of its brittleness due to its high crystallinity. On the other hand, the copolymer of (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV) is widely used due to its flexibility, because of its lower crystallinity [4,5]. Dielectric relaxation spectroscopy (DRS) is sensitive method to investigate the mobility of dipolar groups in the polymer chains [6]. Study of both dielectric constant and dielectric loss in temperature-frequency domain is one of the convenient methods to study the polymeric structure [7]. The aim of this present work is to shed light on the dielectric relaxation and AC conductivity of Poly (hydroxyl butyrate) and its copolymer in a wide range of frequency and temperature.

Experimental Work

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), with three HV concentrations, PHB-5wt% HV, PHB-8wt% HV, PHB-12wt% HV are supplied from (Aldrich chemical company, USA). The samples under investigation for dielectric measurements are placed as thin films between two copper electrodes. First, the samples are melted at the melting temperature on one of the electrodes. Second, the spacers are added to the sample then the other electrode is added. Third, the sample and electrodes are quenched to the room temperature.

The dielectric measurements are carried out in the frequency range 10^{-2} - 10^7 Hz and temperature range 273 - 353 °K, using commercially device supplied by NOVOCONTROL, GmbH, (Germany).

Results and Discussion

Permittivity:

The dielectric relaxation spectroscopy is sensitive to dipole moment orientation in materials under applying AC field. Hence, the rotation of small groups in polymer

chain having a dipole moment could be investigated using dielectric spectroscopy [8]. The polymer materials exhibit different behaviors depending on frequency and temperatures [9]. A typical dielectric spectrum, dielectric constant (ϵ'), of pure PHB and PHB- 12wt%VH as a representative sample of its copolymer is investigated in a wide range of frequency and fixed temperatures, as shown in Fig. 1.

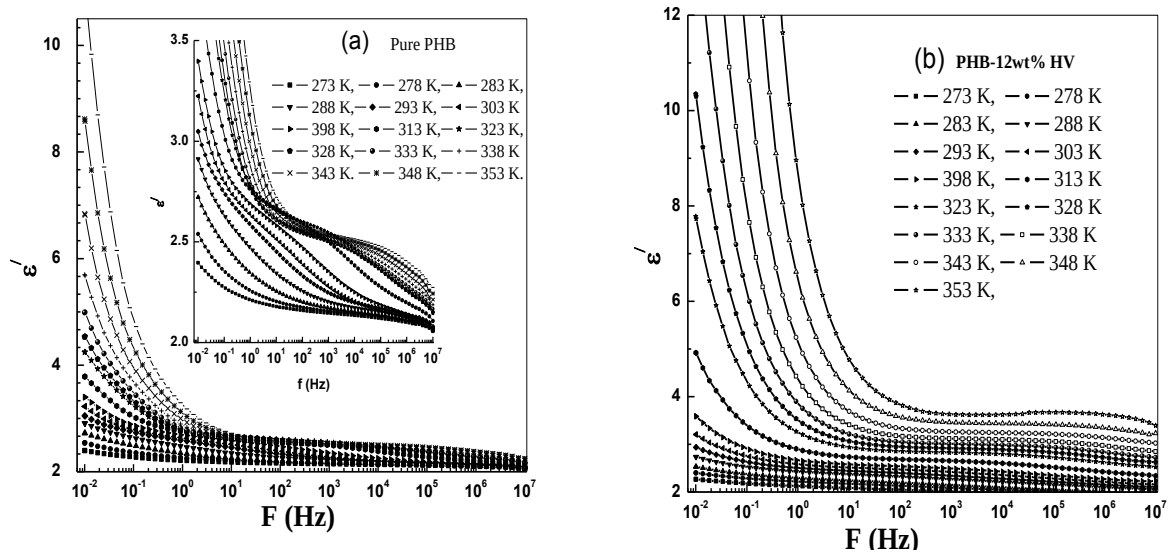


Fig. 1: The dielectric constant ϵ' of (a) pure PHB and (b) PHB-12wt% HV copolymer

As already well known, the behavior of dielectric constant (ϵ') is different for non-polar and polar polymeric materials. Generally, dielectric constant (ϵ') is independent on temperature in case of non-polar material, whereas, it increases with increasing temperature in case of polar material. In polar polymeric materials, the dielectric constant (ϵ') starts to drop at certain frequency. It is found that, for pure PHB and its copolymer sample the dielectric constant (ϵ') values decrease as frequency increases and display a dispersive behavior at lower frequency. In addition, the dielectric constant (ϵ') increases with increasing temperature. The dipole molecules cannot orient themselves at low temperatures. Hence, when the temperature of the material increases the ration of the number of molecules to effective length of dielectric will decrease and the amount of amorphous material will increase, leading to facilitating of dipole orientation and this increases the dielectric constant. The temperature dependence of dielectric constant indicates to orientational distribution of the polymer chains in the crystalline and amorphous regions through the material [10,11]. With increasing temperature, mobility of the dipoles increases due to the increase in specific volume of the material and number of the polar C=O and methyl, CH₃, groups becomes free to orient, leading to an increase of dielectric constant (ϵ') values [12]. On the other side, higher values of dielectric constant (ϵ')

at lower frequencies are indicated to the accumulation of charge carriers at the interface between the samples and electrodes, i.e., space charge relaxation or interfacial polarization. Lower values of dielectric constant (ϵ') values at higher frequencies can be related to electrical relaxation, but at the same time the material electrode polarization cannot be ignored.

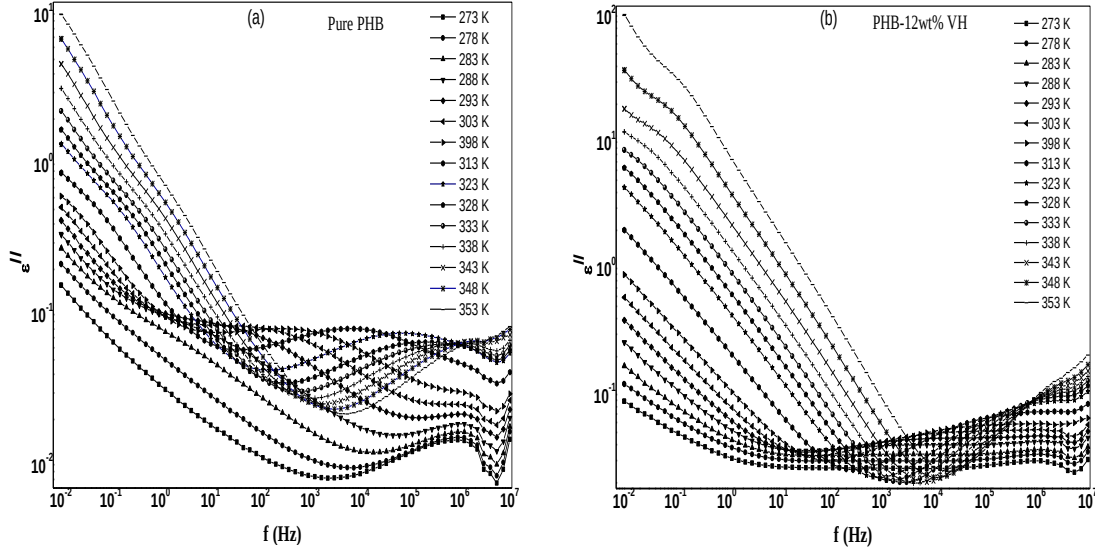


Fig. 2: Dielectric loss (ϵ'') as a function of frequency at fixed temperatures for **(a)** pure PHB and **(b)** PHB-12wt% HV copolymer.

Fig. 2 shows the variation of dielectric loss (ϵ'') of pure PHB and PHB-12wt%HV with frequency at fixed temperatures. It is observed that, this behavior is characterized by a loss peak at high frequency side and it is related to α -relaxation. The origin of this loss peak is the micro-Brownian cooperative motions of the main chain backbone and related to glass transition temperature (T_g) of pure PHB. On the other hand, the copolymer sample is characterized by an additional relaxation observed at higher temperature and very low frequency as a shoulder. This relaxation is attributed to the contribution of ionic conductivity to the dielectric measurements. Fig. 3 shows the variation of dielectric loss (ϵ'') of pure PHB with temperature at fixed frequencies. One can see that, this behavior is characterized by a loss peak in the glass transition temperature region, i.e., α -relaxation, which is attributed to large conformational rearrangement of the main chain in the amorphous region of the material. This behavior is a characteristic to dipolar relaxation. An additional peak is observed in high temperature region and can be assigned to Maxwell-Wagner-Sillars (MWS) interfacial polarization. The origin of this relaxation peak is from the charge carriers build-up created by contact of amorphous and crystalline phases of different conductivities.

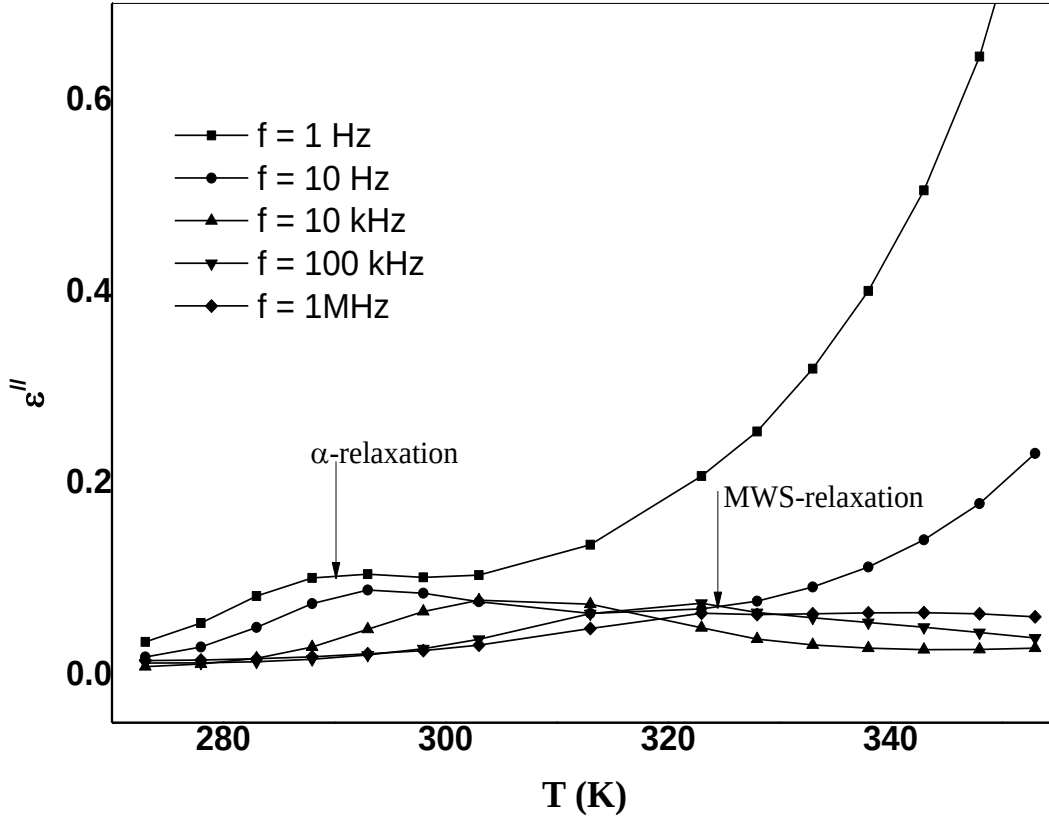


Fig. 3: Isochronal plot dielectric loss (ϵ'') against temperature at fixed frequencies for pure PHB.

Electric Modulus:

The complex electric modulus is used to suppress the electrode effect. The advantage of using electric modulus to investigate the bulk relaxation in polymers and composites materials is that the variation of both dielectric constant (ϵ') and dielectric loss (ϵ'') will minimize. So, the effects of electrode nature, space charge injection and absorbed impurity conduction can be resolved or ignored [13-18]. The formalism of electric modulus gives more information about the mechanism of conductivity relaxation in the temperature-frequency domain in many polymers and polymer composites. The electric modulus M^* , is defined by the following expression as follows [19]:

$$M^* = \frac{1}{\epsilon^*} = M' + iM'' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (1)$$

Where, M' and M'' , ϵ' and ϵ'' are the real and imaginary parts of the complex electric modulus and dielectric permittivity, respectively. Fig. 4 displays the imaginary parts

of electric modulus (M'') versus frequency at different temperatures of pure PHB and PHB-12 wt% HV, as a representative sample of copolymer samples.

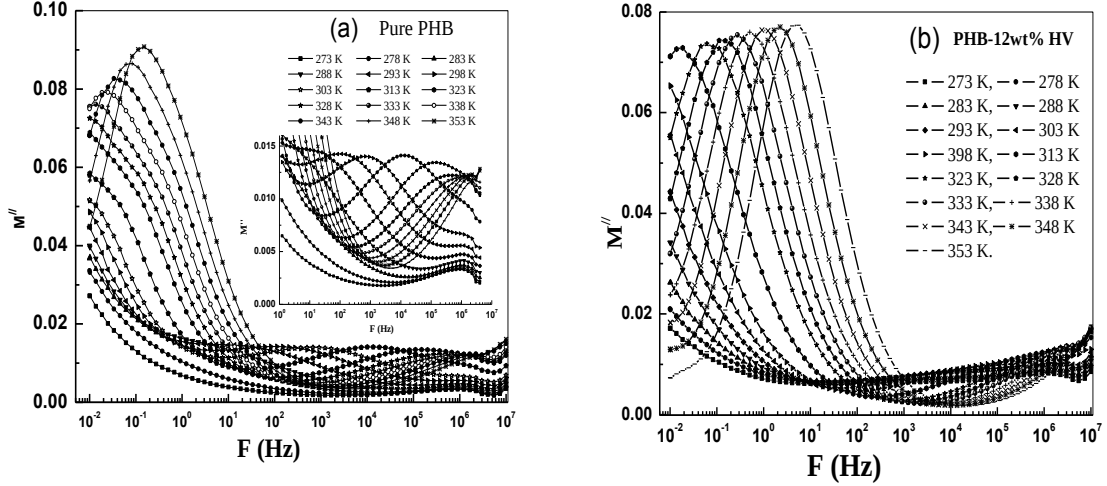


Fig. 4: The imaginary part of electric modulus (M'') versus frequency of (a) pure PHB and (b) PHB-12wt% HV copolymer

It is observed that, the relaxation behaviour of the samples is distinguished by two different relaxation peaks in low and high frequency regions. The first relaxation peak is detected in the frequency range (0.01-1 Hz) and (0.01- 30 Hz) for pure PHB and PHB-12wt% HV copolymer sample, respectively. This relaxation peak shifts to higher frequencies with increasing temperatures. The frequency shift of maximum M'' with increasing temperatures corresponds to the so-called conductivity relaxation [16]. This shift indicates that, the motion of charge carriers becomes faster, leading to a decrease in the relaxation time with increasing temperature. On the other hand, α -relaxation peak is detected as a broad peak in the frequency range (10^2 - 10^6 Hz), as shown in the inset of Fig. 4a. Such broadness in α -relaxation which is observed in M'' spectra for all samples at high frequency side can be interpreted as a consequence of relaxation times distribution. An additional peak is observed as a shoulder at very low frequency $f \sim 0.01$ -0.1 Hz, as shown in Fig. 4a. This peak could be attributed to the accumulation of charge carriers and assigned as Maxwell-Wagner-Sillars (MWS) interfacial polarization.

The dynamics of all relaxation mechanisms of the samples under investigation is represented in Fig. 5. The frequency of the relaxation peak (f_{max}) in the low frequency region defines the conductivity relaxation time (τ). At frequencies lower than f_{max} the charge carriers can make long range order, whereas, at frequencies higher than f_{max} the charge carriers are spatially confined and make localized motion. Hence, in this transition region the charge carriers have the change from long range to short range mobility along the conductivity paths [20,21]. Values of relaxation time are calculated using the empirical formula, $\tau = 1/2\pi f_{max}$ and summarized in Table 2. The values of activation energy of pure PHB and its copolymers are calculated and listed in Table 1, by knowing the slope of $\ln \tau$ against $1/T$ plot, as shown in Fig. 5, using Arrhenius equation as follows:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (2)$$

Where τ_0 , E_a , k_B are the pre-exponential factor, activation energy and Boltzmann's constant, respectively.

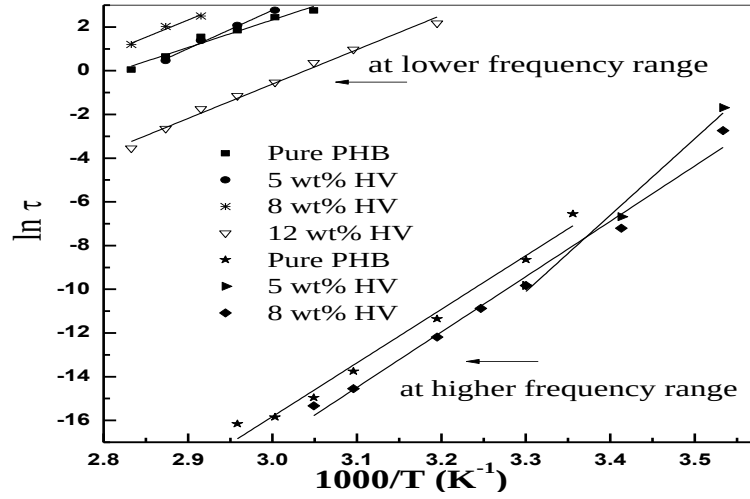


Fig. 5: $\ln \tau$ versus $1000/T$ of pure PHB and its copolymers.

Table 1: Activation energy values (E_a) of Pure PHB and its copolymers in low and high frequency regions.

Sample	Low frequency region E_a (eV)	High frequency region E_a (eV)
Pure PHB	1.09	2.11
5 wt% HV	1.51	3.01
8 wt% HV	1.36	2.18
12 wt% HV	1.35	---

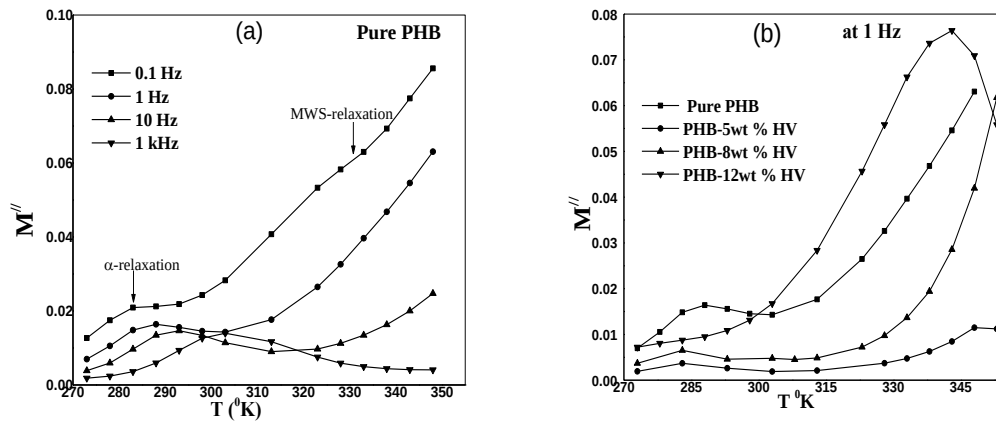


Fig. 6: The imaginary part of electric modulus (M'') versus temperature (T) (a) of

pure PHB at different frequencies and (b) of pure PHB and its copolymers at $f = 1$ Hz.

Fig. 6a displays the variation of M'' as a function of temperature at different frequencies, for pure PHB Fig. 6b displays the variation of M'' as a function of temperature for pure PHB and its copolymer samples at $f = 1$ Hz. Generally, the behavior of pure PHB and its copolymer samples is characterized by a loss peak around ~ 288 °K, which is attributed to the orientation related to the main chain as it is associated with the glass transition temperature (T_g), i.e., α -relaxation of pure PHB. This transition occurs in the amorphous region of the polymer with the initiation of the micro Brownian motion. On the other hand, another loss peak is detected at temperature larger than glass transition temperature of pure PHB around ~ 338 °K, and could be assigned as Maxwell-Wagner-Sillars (MWS) relaxation [22]. The MWS interfacial polarization process exists in the heterogeneous systems due to the difference in conductivities and permittivities of the constituents through the material [23]. The MWS interfacial polarization needs more time in comparison with the electronic polarization. Such behaviour is observed in semi crystalline polymeric materials [12,24].

Fig. 7 displays the dependence of imaginary part of electric modulus $M''(\omega)$ on the real part of electric modulus $M'(\omega)$ of pure PHB and PHB-12wt% HV, as a representative sample of the copolymer, at different temperatures. It is observed that, in M'' against M' plot, the values proceed from lower frequencies to higher frequencies. Each spectrum, i.e., (Cole-Cole diagram), displays a compressed semicircle in the high frequency side and an inclined straight line in the low frequency side. Semicircular behavior is characteristic of Debye behavior for small rigid molecules and molecular liquids [25,26]. The existence of semicircle indicates that, there is no electrode reaction at the electrode interfaces, and only the effects of conductivity relaxations are observed. In addition, the existence of straight line after the semicircle is due to the migration of ions and/or the surface inhomogeneity of the electrodes [27,28].

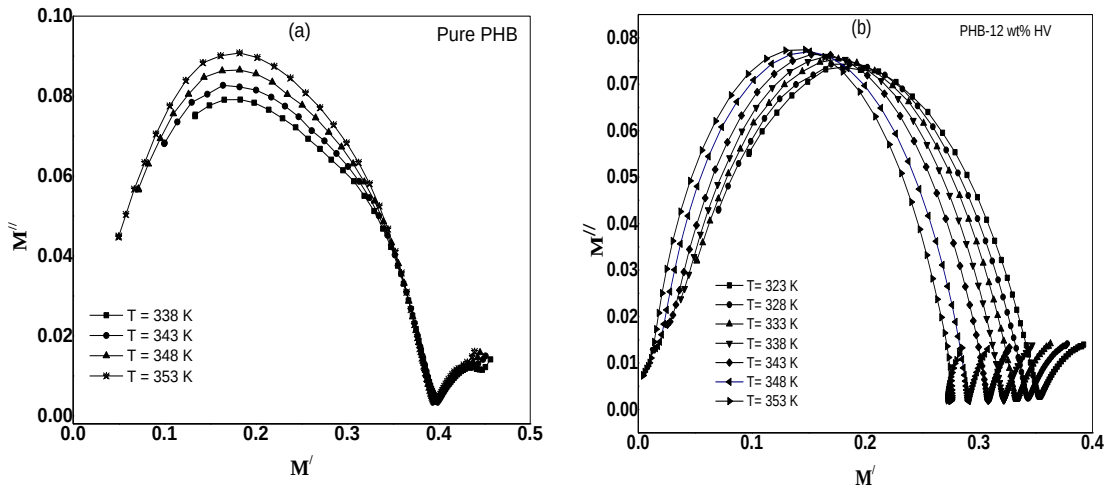


Fig. 7: Dependence of imaginary part of electric modulus $M''(\omega)$ on the real part of

electric modulus $M'(\omega)$ of (a) pure PHB and (b) PHB-12wt% HV at fixed temperatures.

AC Conductivity:

The electrical conductivity dependence on temperature is carried out to investigate the mechanism of charge transport in the polymeric materials. Fig. 8 (a & b) shows the AC conductivity behavior of pure PHB and PHB-12wt% HV copolymer, in a wide range of frequency at fixed temperatures. It is observed that, the electrical conductivity is low at lower frequency due to high energy barriers of the charge carriers which have high relaxation time. On the other hand, the electrical conductivity is increased with increasing frequency because of increment number of charge carriers with low barrier heights, which respond easily at higher frequency.

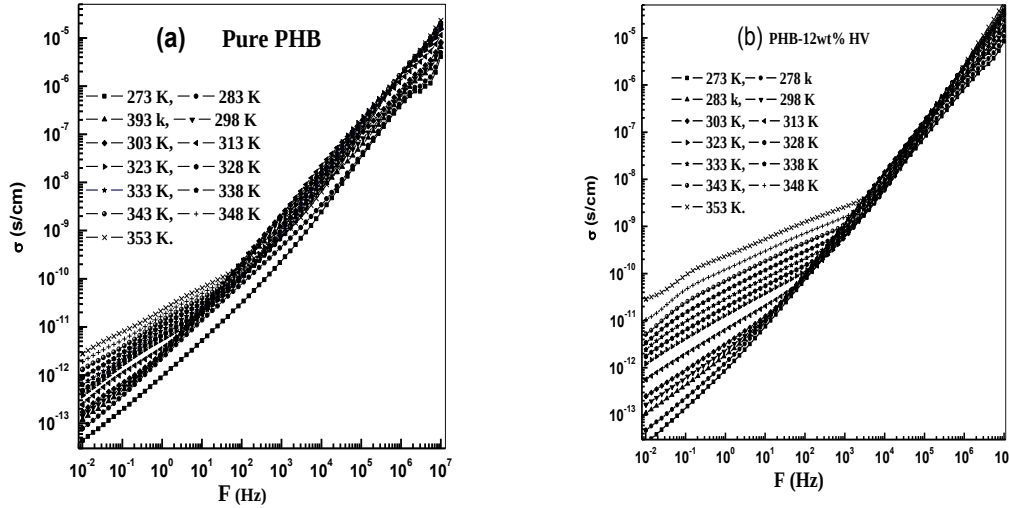


Fig. 8: AC conductivity of a) pure PHB and b) PHB-12wt% HV copolymer.

Generally, the dependence of AC conductivity on frequency at fixed temperature follows a power law behavior (Joncher's universal law) and can be expressed as follows [29]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad (3)$$

Where ω , σ_{dc} , A and n are angular frequency, dc conductivity, temperature-dependent constant and an exponent depends on both frequency and temperature, respectively. The interaction between all the charge species, especially in the polarization processes, is characterized by the parameter n , which can be calculated using the slopes of the $\log(\sigma_{ac})$ against $\log f$ curves at different temperatures. The values of n of all samples are estimated and tabulated in Table 2. The temperature dependence of the parameter n can be explained on the basis of the many-body interaction model. At

higher temperatures, the interaction between neighboring dipoles is negligible, and only the conductive element is the DC resistance [30].

Table 2: The values of both relaxation time (τ) in low and high frequency regions and n parameter.

T (K)	Pure PHB $\tau_{low}(sec), n, \tau_{high}(sec)$	PHB-5 wt% HV $\tau_{low}(sec), n, \tau_{high}(sec)$	PHB-8 wt% HV $\tau_{low}(sec), n, \tau_{high}(sec)$	PHB-12 wt% HV $\tau_{low}(sec), n, \tau_{high}(sec)$
273	---, 0.20, ---	---, 0.47, ---	---, 0.22, ---	---, 0.24, ---
278	---, 0.21, ---	---	---	---, 0.25, ---
283	---, 0.21, ---	---, 0.46, 1.20x10 ⁻⁰¹	---, 0.23, 3.8x10 ⁻⁰²	---, 0.26, ---
288	---, 0.22, ---	---	---, 0.24, 7x10 ⁻⁰⁴	---, 0.27, ---
293	---, 0.23, ---	---, 0.46, 1.25x10 ⁻⁰³	---, 0.25, ---	---, 0.27, ---
298	---, 0.53, 0.24x10 ⁻⁰³	---	---	---, 0.28, ---
303	---, 0.59, 0.25x10 ⁻⁰³	---, 0.48, 5.40x10 ⁻⁰⁵	---, 0.25, 5.40x10 ⁻⁰⁵	---, 0.29, ---
313	---, 0.66, 0.26x10 ⁻⁰⁵	---, ---, 3.92x10 ⁻⁰⁶	---, 0.26, 5.10x10 ⁻⁰⁶	8.84, 0.30, ---
323	---, 0.71, 0.28x10 ⁻⁰⁶	---	---, 0.26, 8.12x10 ⁻⁰⁷	2.61, 0.31, ---
328	---, 0.75, 0.28x10 ⁻⁰⁷	---, 0.48, ---	---, 0.27, 3.70x10 ⁻⁰⁷	1.44, 0.32, ---
333	12.24, 0.29, 1.31x10 ⁻⁰⁷	12.24, ---, ---	---, 0.27, 1.29x10 ⁻⁰⁷	0.58, 0.33, ---
338	6.37, 0.29, 9.65x10 ⁻⁰⁸	7.58, ---, ---	---, 0.28, 5.89x10 ⁻⁰⁸	0.32, 0.33, ---
343	4.82, 0.29, 7.14x10 ⁻⁰⁸	3.31, ---, ---	12.24, 0.28, ---	0.17, 0.34, ---
348	1.91, 0.30, ---	1.50, ---, ---	5.68, ---, ---	0.07, 0.34, ---
353	1.05, 0.30, ---	1.16, ---, ---	2.56, ---, ---	0.03, 0.35, ---

The analysis of AC electrical conductivity in a wide range of frequencies is carried out to investigate the electrical transport in the polymeric material. The AC measurements are expected to give more information about the conduction mechanism at temperatures below and above the glass transition temperature (T_g). Fig. 9 shows the Arrhenius plots of the real part of the AC electrical conductivity, i.e., $\ln \sigma$ versus $1/T$, at different frequencies, using the following equation:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

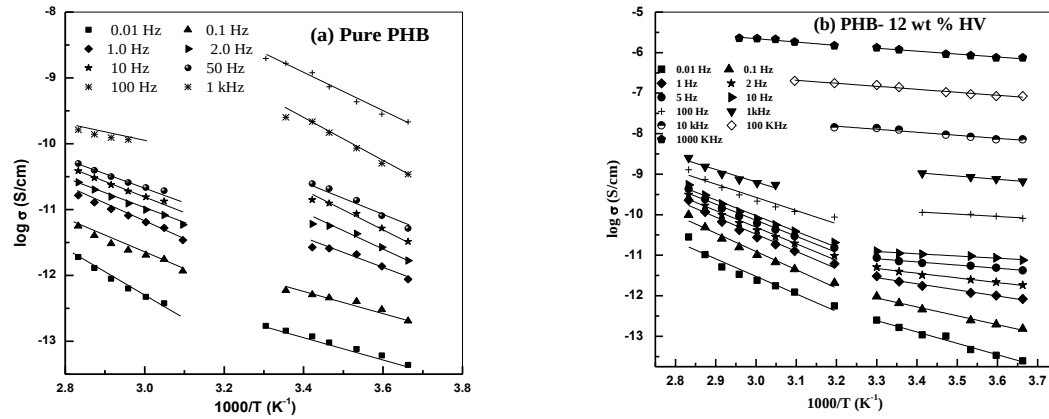


Fig. 9: $\log \sigma$ versus $1/T$ of a) pure PHB and b) PHB-12wt% HV.

It is observed that, Arrhenius plots are characterized by two different regions in low and high-temperature region with different slopes. The results indicate that there is a change in the transport mechanism around glass transition temperature region (T_g). It is found that, the activation energy values are decreased with increasing frequency. The activation energy values are estimated as a function of frequency and summarized in Table 3.

Table 3: The activation energy values of pure PHB and copolymer samples.

f (Hz)	Pure PHB			5 wt% HV			8 wt % HV			12 wt % HV		
	E_{a1}	E	a_2	E_{a1} (eV)	E	a_2	E_{a1}	E	a_2	E_{a1}	E	a_2
	(eV)	(eV)			(eV)		(eV)	(eV)		(eV)	(eV)	
0.01	0.14	0.29		0.16	0.45		0.39	0.51		0.24	0.37	
0.1	0.12	0.19		0.08	0.35		0.09	0.38		0.19	0.39	
1	0.18	0.18		0.03	0.27		0.04	0.33		0.13	0.37	
2	0.20	0.18		0.03	0.25		0.05	0.31		0.09	0.35	
5	0.23	0.19		0.03	0.22		0.08	0.29		0.07	0.34	
10	0.25	0.17		0.09	0.20		0.10	0.27		0.05	0.33	
100	0.26	0.11		0.08	0.06		0.20	0.20		0.04	0.28	
1000	0.25	--		0.24	--		0.27	--		0.07	0.26	
10kHz	--	--		0.20	--		0.26	--		0.06	--	
100kHz	--	--		0.12	--		0.19	--		0.06	--	
1000kHz	--	--		0.05	--		0.13	0.06		0.06	0.07	

Conclusion

The dielectric constant (ϵ') of pure PHB and its copolymer (3-hydroxybutyrate-co-3-hydroxyvalerate), PHB-HV, is investigated in wide range of frequency from 0.001 Hz to 1×10^7 Hz and in range of temperature from 273 °K to 353 °K. It is observed that, pure PHB and its copolymers are characterized by high dielectric constant at low

frequency and high temperature. This behavior is attributed to interfacial polarization, (Maxwell-Wagner-Sillars) polarization. The behavior of imaginary part of electric modulus (M'') as a function of frequency for all samples is carried out to suppress the electrode effect. It is found that, this behavior is distinguished by two relaxation regions in low and high frequency. In addition, the behavior of (M'') with temperature for the samples is characterized by two different relaxation peaks. The first one is positioned in the region of T_g of pure PHB, whereas, the second peak at temperature ~ 338 °K, and is assigned as Maxwell-Wagner- Sillars (MWS) relaxation. AC electrical conductivity of all samples is investigated. The Arrhenius plots of AC conductivity showed a remarkable change in the conduction mechanism in glass transition temperature region of pure PHB.

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