DIELECTRIC RELAXATION OF POLY(β -HYDROXYBUTYRATE) RELATING TO MICROSTRUCTURE.

I. Šics*, V. Tupureina*, M. Kalniņš*, T.A. Ezquerro, F.J. Baltá-Calleja

Instituto de Estructura de la Materia, C.S.I.C. Serrano 119, Madrid 28006, Spain.

*Riga Technical University, Institute of Polymer Materials,

Azenes 14, Riga LV 1048, Latvia.

Abstract

The dielectric relaxation behaviour of a high molecular weight Poly(β -hydroxybutyrate) (PHB) synthesised through *Azotobacter Chroococcum* 23, was investigated by measuring the complex dielectric permittivity over a wide frequency and temperature range. PHB exhibits two dielectrically active processes in the temperature and frequency range investigated. The higher temperature relaxation (α) has been attributed to motions appearing at temperatures above the glass transitions temperature (T_g). The low temperature process (β) is thought to be due to local motion of carboxyl groups and local rotations around the C-O bond. The phenomenological Havriliak-Negami (HN) description has been applied to analyse the dielectric loss data and to extract the shape parameters of the above relaxations in an attempt to correlate experimental data to dynamics of relaxation processes.

Introduction

Poly(β -hydroxybutyrate) (PHB) is a stereoregular biopolyester produced by many bacterial strains as a carbon and energy reserve. Its chemical structure is shown to be:

PHB is a linear thermoplastic polymer which in contrast to synthetic polymers has a fundamental advantage of coming from renewable resources. Moreover it is truly biocompatible and biodegradable being completely digested and metabolised by a wide variety of bacteria and fungi, making it extremely interesting for many applications. There have been a large number of investigations carried out on the synthesis and biochemical, physical and chemical properties since it was discovered in 1927 by M. Lemoigne [1]. An exhaustive overview on the properties of PHB can be found in the literature [1].

At the same time PHB did not yet find wide, real application in any of the potential areas. It seems that there is still no pathway, effective enough and perspective from a commercial point of view, to overcome certain of the technological drawbacks of this linear polyester: long secondary crystallization time, embrittlement of material upon physical ageing, and narrow processing temperature window. Many of the possible applications of polymers depends on their ability to dissipate energy. Depending on temperature, energy can be dissipated by the primary relaxation (α) through molecular segmental motions for $T > T_g$ or by local motions giving rise to secondary relaxations ($\beta, \gamma, \dots$) for $T < T_g$.

To our knowledge, there have been relatively few reports describing relaxational processes in PHB from dynamic mechanical experiments and even less from electrical property analysis [2-5]. Electrical properties related studies on PHB have been mostly concerned with piezoelectricity and its related effects [2]. Three relaxational processes are usually

observed in PHB as reported by various authors[2,4], the ambient temperature relaxation being usually associated to the T_g , while there are distinct opinions on sub-ambient and high temperature process assignment. Scandola *et al.* propose that a sub-ambient relaxation originated in the presence of absorbed water in PHB material [3]. The most recent work of Pratt and Smith [4] discusses this assignment, comparing secondary relaxations in other polyesters and concluding the major role of methyl and ester groups. An influence of possible phosphite residues in PHB samples on the sub-ambient relaxation is proposed. The high-temperature process has been attributed to the ionic DC conduction process [2] or constrained motions in the PHB crystalline phase [4].

The purpose of the present work is to shed light on the molecular relaxation processes in PHB by measuring the complex dielectric constant in a wide frequency and temperature range. This allows to analyze relaxation processes in terms of existing phenomenological models, something that was not yet done for PHB.

Experimental

Materials

PHB prepared by continuous fermentation of producer *Azotobacter Chroococcum* 23 was investigated. The methodology of fermentation for this specific bacteria has been described before [6].

PHB was extracted by chloroform and purified by consecutive filtration in chloroform and reprecipitation with isopropanol. Films of the pure polymer with an average thickness of about 40 μm were prepared by casting from chloroform solutions under slow evaporation conditions at room temperature. After casting, the film was kept overnight in vacuum at room temperature to remove traces of solvent.

The average molecular weight of the sample was estimated from viscosity measurements. The known Mark-Houwink equation $[\eta]=K \times M^\alpha$ was employed, where $K=1.18 \times 10^{-4}$ and $\alpha = 0.78$ for this specific polymer-solvent system [7]. Measurements were performed on the PHB solutions in chloroform using an Ubbelohde capillary viscometer immersed in a thermostated bath at 30°C temperature. An average molecular weight $M_v = 1.5 \times 10^6$ g/mol was estimated.

Techniques

Calorimetric measurements were carried out using a Perkin-Elmer DSC-7 scanning calorimeter. Calibration was made by using indium and zinc standards. Samples were scanned with a heating rate of 20 °C/min in the temperature range from -25°C to 190°C.

Wide angle X-ray diffraction (WAXD) experiments were performed using a Rigaku goniometer at room temperature and Ni filtered CuK α radiation from a Rigaku rotating anode generator.

Complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) measurements were performed in the frequency range of 10^{-1} - 10^5 Hz using a Novocontrol apparatus including impedance analyser and measurement cell. For this purpose the films were provided with circular gold electrodes 3cm in diameter using a sputtering technique and placed between two gold-plated stainless steel electrodes. The accuracy in temperature during the measuring time was estimated to be $\pm 0.1^\circ\text{C}$.

Results

Calorimetry.

Thermograms of the PHB specimen under investigation in the temperature range from -25°C to 190°C are shown in fig 1. It is known that PHB is a semicrystalline polymer exhibiting a

glass transition temperature T_g near 0°C depending on the crystalline content, origin and some other factors. There have been previous reports on several melting endotherms in PHB and its copolymers [5,8], usually attributed to the melting of different crystal populations. The appearance of endothermic peaks at $T_2=168^\circ\text{C}$, $T_3=175^\circ\text{C}$ evidences the melting of PHB crystals (Fig. 1a). An estimation of the weight percent crystallinity was made considering the area under the melting endothermas normalized by the sample mass. By taking $\Delta H_m = 146 \text{ J/g}$ [9] as the value for the 100 % crystalline PHB, the crystallinity was estimated to be 62 %. The slight shoulder at T_1 is usually attributed to the reorganisation of poorly ordered crystals by recrystallization and does not appear in annealed samples [5]. The shoulder of the DSC curve at T_1 starts at temperatures where cold crystallization occurs during the second scan, confirming the recrystallization origin of the process.

Owing to the high crystalline content in the solution cast films and the restrictions imposed to the amorphous fraction the evaluation of T_g in the semicrystalline material was not possible. The glass transition temperature was estimated from the second heating run, performed on glassy PHB after quenching the sample from the molten state (Fig. 1b). T_g was found to be 2°C.

Wide Angle X-ray Diffraction.

The X-ray diffractogram of the investigated crystallized PHB (see Fig. 2) evidences the presence of well defined Bragg peaks superimposed over an amorphous halo. The crystalline reflections correspond to the orthorhombic unit cell of poly(β -hydroxybutyrate) [10].

The weight fraction crystallinity was estimated from the ratio between the crystalline peaks to the total area of coherent scattering after subtraction of the background [11,12]. Separation of the crystalline peaks from the amorphous halo was done by assuming Voigt functions for the scattering maxima [13]. The value of crystallinity was estimated as 55

wt%. The slight discrepancy between DSC and WAXD data is often observed and may be accounted for as the error introduced by the separation procedure due to the uncertainty in the shape of the amorphous halo.

Dielectric Relaxation Measurements of the semicrystalline PHB.

The plots of dielectric loss, ϵ'' , and dielectric constant, ϵ' , values as function of temperature and frequency for the investigated sample are presented in Fig. 3. The dielectric measurements clearly reveal the existence of two relaxation processes in the investigated temperature range. We will refer to them as β and α in order of increasing temperature. Both relaxation processes appear as maxima in the dielectric loss measurements (fig.4a) and as concurrent steps in the dielectric constant plots (fig.4b). The intensity and shape of both processes is obviously different, the α - process being stronger and its distribution over the frequency and temperature range being much narrower than that of the β - process. The steep rise of the loss values at higher temperatures is ascribed to the onset of the conductivity process.

Discussion.

β and α -processes.

Three relaxational processes are usually observed in PHB as reported by various authors [2-5]. The loss peak positions for β - and α - processes reported agree quite well with our observations.

A high temperature relaxation, missing in our dielectric loss data, (71°C at 0.1 Hz) reported by Pratt *et al.* [4] and ascribed to the Maxwell-Wagner-Sillars (MWS) interfacial polarisation, is often observed in heterogeneous systems at lower frequencies. Actually one can detect a shoulder starting at approximately 80°C (0.1 Hz) in the dielectric constant

curves (see Fig.3b). This would indicate the occurrence of a dielectrically active process which is overlapped by high dc conductivity (σ).

The other possible explanation for the increase of ε' and ε'' at high temperatures and low frequencies could be the increase of the average dipole moment as a result of the increasing amount of amorphous material. This explanation could be supported by the presence of the slight step T_1 in the DSC curve (Fig.1a) at around 76°C. If part of the poorly organised crystals melts, and does not recrystallize immediately, this would lead to a slight, temporary increase of the amorphous fraction yielding an increase of both the dielectric constant ε' and dielectric loss ε'' .

The maximum position of the loss peak maxima for both relaxations (β and α) shifts towards higher temperatures, at different rates, as frequency increases and tends to merge at higher frequencies.

The frequencies of the maximum loss, $F_{\max}$, for the β and α -processes are represented in Fig. 5 as a function of the reciprocal temperature. These values have been derived from the isochronal plots of ε'' vs. temperature of Fig. 4. The difference in the frequency dependence of both processes is well seen. The β -process can be satisfactorily described by a straight line, exhibiting an Arrhenius behaviour as observed for relaxations corresponding to small scale local motions [14]. The α -relaxation is somewhat skewed towards higher temperatures implying the more complex nature of the process.

It is widely accepted [14] that relaxation process connected with the onset of large scale Brownian motion above T_g in polymers follows a Vogel-Fulcher-Tamann (VFT) type behaviour, and thus activation energy cannot be directly obtained. Our experimental data were fitted to the VFT equation in the form proposed by Angell [15]:

$$\log (F_{\max}) = -DT_0/(2.303(T-T_0)) + B \quad (1)$$

where T_0 is described as the ideal glass transition temperature, B is a material constant and D is Angell's introduced parameter called fragility strength [16]. In the phenomenology proposed by Angell, the parameter D characterizes the extent of non-Arrhenius behaviour, classifying materials between "strong" ($D = 100$) and "fragile" ($D \approx 2$) glass formers. "Strong" glass formers obey Arrhenius law and are materials which in the glassy state form a three-dimensional network of strongly directional bonds. On the other hand "fragile" glass formers form weaker, less directional bonds. According to Angell, the physical meaning of the parameter D can be derived from Adam-Gibbs theory concerning the cooperative relaxation in densely packed liquids. The parameter D is related to the density of the minima of potential energy surface of system and to the barrier heights between the minima. Polyisobutylene (PIB) is considered up to now as the strongest polymer with $D \approx 16$ [16] while a value as low as $D \approx 2.7$ has been reported for Poly(2-hydroxypropyl ether Bisphenol A)(PH) [17]. It has been proposed that polymers having rigid backbones would be located on the fragile side, i.e. low values of D , while those polymers with less rigid chain backbones would exhibit higher D values [18].

In our case the fitting yielded values of the parameters $T_0 = 223.2$ K, $B = 12.9$ and $D = 7.9$ for the α -relaxation. In the present study the value of the parameter D shows that PHB in its amorphous state can be attributed to the intermediate fragile polymers. This can be explained by the chemical structure of the PHB molecule where every third backbone bond is C-O, making the backbone chain more flexible than that of PH.

Phenomenological analysis of the results.

The phenomenological model due to Havriliak-Negami (HN) [19] was employed to characterize the relaxation processes in the frequency domain. Figure. 6 shows some of the dielectric loss curves as a function of frequency which were centered in the frequency window of our equipment. Experimental data were fitted to the HN equation in the form of Cole-Cole plots (Argand plots). Symbols represent experimental data and solid curves were calculated according equation (2).

$$\varepsilon^*(\omega) - \varepsilon_{\infty} = \frac{\varepsilon_0 - \varepsilon_{\infty}}{\left[1 + (i\omega\tau_0)^b\right]^c} \quad (2)$$

where ε_0 and ε_{∞} are the relaxed and unrelaxed dielectric constant values, τ_0 is the central relaxation time, $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{\infty}$ is the dielectric strength of the process, ω is the angular frequency ($\omega = 2\pi F$, F is the frequency) and b and c are shape parameters ($0 < b, c \leq 1$) describing symmetrical and asymmetrical broadening of relaxation time distribution function. In case of a symmetrical loss peak ($c = 1$) the HN equation yields the Cole-Cole expression, and if $b = c = 1$ the well known Debye's single relaxation case is restored. Fitting of the experimental data to the HN equation was done as previously reported [20]. The values of the parameters obtained by fitting the experimental points to equation (2) are presented in Table 1. for the case of the α - relaxation process.

The value of parameter c , close to unity, shows that the distribution of relaxation times is symmetric. This is characteristic of semicrystalline polymers in which a symmetrical distribution of relaxation times is frequently observed. Schlosser & Schönhals [15,21] proposed a model introducing two new parameters $n = bc$ ($0.5 \geq n > 0$) and $m = b$, where m governs the slope of the low frequency side of the dielectric loss curve and is connected with local chain dynamics of the polymeric solid. The n parameter is related to the slope of

high frequency side of ε'' vs. $\log F$ plot and according to the theory of Schlosser & Schönhals, describes intermolecular correlation of the segments of different chains (large scale cooperative motions). Small values of the m parameter (see table 1.) indicate the occurrence of restrictions to the large scale molecular motions. Taking into account the relatively high degree of crystallinity of the PHB samples, the low m value can be explained by the influence of the crystallites, constraining the free movements of adjacent macromolecules and lowering their flexibility in the amorphous phase. The temperature dependence of parameters follows the behaviour predicted by the Schlosser & Schönhals model. The values of the m and n parameters gradually increase with temperature indicating a decrease of the intermolecular interaction and, consequently, a reduction of the hindrance to both local and extended mode motions. This result seems reasonable as macromolecules become more flexible with increasing temperature. Table 1 also evidences a slight increase of dielectric strength values with temperature suggesting an increase of the amount of active dipoles participating in the relaxation process.

Dielectric loss of secondary relaxations in polymers generally possess a wide and symmetrical distribution of relaxation times. Experimental points were fitted to equation (2) leaving the parameter $c = 1$ in order to yield symmetrical curves. The best fits can be visualized in Fig. 6 and the fitting parameters are summarised in Table 2. The small value of the parameter $b \approx 0.23$ implies a broad distribution of relaxation times, as expected for secondary relaxations.

Usually the low temperature relaxation in polyesters is ascribed to the local motions of carboxyl groups [22,23] and macromolecule chain ends. Activation energies (E_A) for those relaxations of ≈ 54 kJ/mol have been previously reported in literature[14]. It is not likely that the influence of motions from chain-end groups in case of PHB β -relaxation could be

very strong considering the very high degree of polymerisation i.e. the very low concentration of chain-end groups of this bacterial polyesters.

The activation energy (E_A) for the β -process in our PHB was calculated from the data of Fig. 5, yielding a value of 51 ± 4 kJ/mol. This coincides quite well with the E_A value for the β -process in PHB reported by Pratt and Smith (55 kJ/mol) [4].

PHB usually contains sorbed water in amounts up to 1 wt% [3,24]. It is known that sorbed water also exhibits characteristic relaxational spectra at subambient temperatures. According to the data of ref.[23] the dielectric loss due to the water would appear at slightly lower temperatures, overlapping the tail of the PHB originated β -relaxation process, with increasing influence at higher frequencies.

Conclusions

The dielectric measurement of bacterial polyester PHB exhibits mainly two relaxation processes in the investigated temperature range. The higher temperature α -relaxation is attributed to the onset of the large scale cooperative motions at the glass transition, characterised by a value of the fragility strength parameter $D = 7.9$. Analysis of the molecular mobility of the amorphous fraction of PHB from the shape of dielectric loss curves reveals the occurrence of constrained motions of macromolecules owing to the influence of the crystalline phase. The constraining influence is also evidenced by the very broad and symmetrical relaxation time distribution.

The β and α -processes have been analysed in terms of the Havriliak-Negami model. The activation energy of the β -process $E_A = 51 \pm 4$ kJ/mol is rather close to that usually found in polyesters. The nature of the β -process can be explained in terms of local motions of carboxyl groups, similarly to the low temperature relaxations of other polyesters.

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Figure captions.

Figure 1. DSC thermograms of PHB sample: (a) first scan of solution cast sample, (b) second scan after quenching from the molten state.

Figure 2. Wide angle X-ray diffraction pattern from a PHB film. Dotted lines represent separated peaks from Bragg reflections.

Figure 3. Three-dimensional plot of measured complex dielectric permittivity as a function of temperature and frequency. (a) Dielectric loss values ε'' . (b) Dielectric constant ε' .

Figure 4. Isochronal (constant frequency) plot of: (a) Dielectric loss ε'' vs. temperature. (b) Dielectric constant ε' vs. temperature. Same symbols for both graphs.

Figure 5. Log ($F_{\max}$) as a function of reciprocal temperature (Arrhenius plots) for the secondary (β) and glass (α) transition in semicrystalline PHB. Solid lines are fittings to the Arrhenius and Vogel-Fulcher equations respectively.

Figure 6. Dielectric loss ε'' vs. log F for selected temperatures: a) α -relaxation; b) β -relaxation. Solid lines represent fittings to the Havriliak-Negami equation.

References

1. G. J. L. Griffin Ed., *Chemistry and technology of biodegradable polymers*, Chapman & Hall, London, 1994, p.154
2. Y. Ando and E. Fukada, *J. Polym. Sci., Part B: Polym. Phys.*, 22 1821 (1984).
3. M. Scandola, G. Ceccuroli and M. Pizzoli, *Makromol. Chem., Rapid Commun.*, 10, 47 (1989).
4. G. J. Pratt and M. J. A. Smith, *Eur. Polym. J.*, 33, 857 (1997).
5. F. Biddlestone, A. Harris, J. N. Hay, T. Hammond, *Polym. Int.*, 39, 221 (1996).
6. L. I. Young, E. M. Stegantseva, L. Savenkova and Y. H. Park, *J. Microbiology and Biotechnology*, 5, 100 (1995).
7. S. Brückner, S. V. Meille, L. Malpezzi, A. Cesáro, L. Navarini and R. Tambolini, *Macromolecules*, 21, 967 (1988).
8. R. J. Rule and J. J. Ligat, *Polymer*, 36, 3831 (1995).
9. R. Pearce and R. H. Marchessault, *Polymer*, 35, 3990 (1984).
10. Z. Škrbic and V. Divjakovic, *Polymer*, 37, 505 (1996).
11. D. J. Blundell and B. N. Osborn, *Polymer*, 24, 953 (1983).
12. F. J. Baltá-Calleja and C. G. Vonk, *X-ray Scattering of Synthetic Polymers*, Elsevier, Amsterdam, 1989, p.317
13. H. P. Klug and L. Alexander, *X-Ray diffraction procedures for Polycrystalline and amorphous materials*, Wiley, N.Y., 1974, Chap. 5.
14. N. G. McCrum, B. E. Read and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, N.Y., 1974, p.617
15. A. Schönhals and E. Schlosser, *Colloid Polym. Sci.*, 267, 25 (1989).
16. R. Böhmer, K. L. Ngai, C. A. Angell and D. J. Plazek, *J. Chem. Phys.*, 99, 4201 (1993).

17. A. Alegría, E. Guerrica-Echevarría, L. Goitiandia, Y Tellería and J. Colmenero, *Macromolecules*, 28,1516 (1995).
18. K.L. Ngai and C.M. Roland, *Macromolecules*, 26, 6824 (1993).
19. S. Havriliak, and S. Negami, *Polymer*, 8, 161 (1967).
20. T. A. Ezquerro, F.J Baltá-Calleja and H.G. Zachmann, *Polymer*, 35, 2600 (1994).
21. A. Schönhals and E. Schlosser, *Colloid Polym.Sci.*, 267, 963 (1989).
22. J. C. Coburn, and R. H. Boyd, *Macromolecules*, 19, 2238 (1986).
23. P. Hedvig, *Dielectric Spectroscopy of Polymers*, Adam Hilger , Bristol, 1977, p.431
24. T. L. Lebedeva, A. L. Iordanskii and A. V. Krivandin, *Polym. Sci. Series A*, 36, 919 (1994).

Tables

Table1. Values of the parameters obtained from the fitting of HN equation to the α -relaxation in PHB.

$T (^{\circ}\text{C})$	Parameters					
	$\Delta\varepsilon$	ε_0	τ_0	$b=m$	c	$bc=n$
10	1.059	5.005	7.9×10^{-2}	0.21	0.95	0.20
15	1.073	5.000	7.0×10^{-3}	0.21	1.00	0.21
20	1.097	4.993	8.8×10^{-4}	0.21	1.00	0.21
25	1.133	4.988	1.3×10^{-4}	0.22	1.00	0.22
30	1.102	4.955	2.5×10^{-5}	0.23	1.00	0.23

Table2. Values of the parameters obtained from the fitting of HN equation to the β -relaxation in PHB.

$T (^{\circ}\text{C})$	Parameters			
	$\Delta\varepsilon$	ε_0	τ_0	b
-90	0.244	4.06	1.07×10^{-6}	0.223
-70	0.253	4.06	2.11×10^{-7}	0.221

Figure.1

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.