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Dielectric relaxation of polyurethane biocomposites

V. E. MUSTEATA, D. FILIP, S. VLAD, D. MACOCINSCHI*

Institute of Macromolecular Chemistry “Petru Poni”, Aleea Grigore Ghica Voda 41A, 700487, Iasi, Romania;

An experimental study using dielectric spectroscopy measurements is made on molecular motions as function of temperature and frequency of polyurethane biocomposites, based on poly(ester urethane) and extracellular matrix components (hydrolyzed collagen, elastin, hyaluronic acid, chondroitin sulfate). Relaxation parameters were evaluated from isothermal dielectric spectra in -100÷-30 ^{o}C temperature interval by applying empirical Havriliak-Negami function. Relaxation times versus temperature were analysed for glass transition and secondary transitions by means of Arrhenius law and Vogel-Fulcher-Tammann-Hesse equation.

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1. Introduction

Supramolecular polymers are an unique class of polymers formed through a spontaneous assembling process due to non-covalent bonds such as hydrogen bonds [1-4]. The supramolecular polymers form the most recent branch of “chemistry beyond the covalent bond” [1]. Generally, intermolecular reversible linkage of the hydrogen bonds type, leads to numerous unusual properties of supramolecular polymers in comparison to the others. So, one gain a possibility to engineer the multi-molecular system, of a given well-defined physical property. In view of type of interactions linking the molecular components together, the supramolecular chains have a dynamical character. So, the dielectric relaxation studies can provide information on the molecular dynamics and equilibration of the dipolar system after its perturbation by an external electric field.

For preparation of the biomedical polymers it is necessary to achieve adequate mechanical properties, biochemical inertia and biocompatibility [5-7]. Evaluation of the biomechanical behaviour of the biocomposites clarifies aspects related to the modifications of the biotissues under strain. Nature of the self-assembled microstructure and chemical bonds, functional particularities of the biotissues are investigated on the basis for modeling of consolidation or replacement. Dielectrical behaviour of the biocomposites determines muscle contraction and is responsible for compatibility of polymer biosystems in contact with blood. In case of anhydrous proteins or with low amounts of water, conductivity is due to electrons, while at a higher amount of adsorbed water conductivity is due to protons. For example, in the case of collagen molecules, any alteration of the triple helix structure will affect conductivity, through breaking of hydrogen bonds, [8-11]. Modification of the amount of the structurated water and dielectrical behaviour is the effect of breaking of the endothelium continuity of the blood vessels under the environment of inorganic ions and polyelectrolytes from blood. After their adsorption the platelets and clot formation are affected. [12-14].

The paper discusses the influence of the extracellular matrix components embedded in a polyurethane matrix on dynamic dielectric properties of the resulted biocomposites.

2. Experimental

2.1. Polymer preparation

Polyurethane (PU) employed in the preparation was synthesized using a two-step polyaddition reaction, as previously described for other polyurethane preparation, [15-17]. The materials used were diphenylmethane 4, 4’-diisocyanate (MDI) freshly distilled, from Merck, poly (ethylene glycol) adipate (PEGA, purity 97 %, MW = 2000 g/mol) and ethylene glycol (EG, purity 95 %) from Fibrex SA Savinesti-Romania. PEGA was dehydrated at 120^{o}C, for 3 h to remove residual water. Briefly, PEGA reacted with MDI at 90^{o}C, under nitrogen atmosphere, for 1 h. In the second stage, the isocyanate groups of the prepolymer reacted with the chain extender (EG) at 60^{o}C. The molar ratio PEGA: MDI: EG was 1:5:4. The obtained polyurethane was precipitated in water and dried under vacuum for several days. The structure of the synthesized polyurethane is as follows: $[\text{MDI-PEGA-(MDI-EG)}_4]_n$ with the weight composition : 60.01 % C, 4.23 % N, 6.16 % H, 29.60 % O; weight-average molecular weight is 141038 and polydispersity index 1.29.

Hydrolyzed collagen (HC) was prepared in the laboratory from bovine derma by acid hydrolysis followed by a spray-drying process using BUCHI 190 Mini Spray Dryer. HC is a peptide mixture with the elemental composition: 42.7 % C, 10.8 % H, 12.2 % N and 34.3 % O, the average molecular weight was 99000, as determined by GPC and its polydispersity was 1.66.

K-Elastin (KEL) was prepared from insoluble elastin powder (calf ligament, Sigma) by stirring in KOH 1 M (in ethanol, 1:4, v/v), at 30^{o}C, for 48 h, neutralizing with acetic acid and dialysis against bidistilled water [18]. The final solution has 1.3 % dry weight and 68.7 % protein content.

Hyaluronic acid (HA, Sigma) was obtained from human umbilical cord and chondroitin sulfate (CS, Sigma) was obtained from bovine tracheal cartilage.

2.2. Polymer biocomposites preparation

Four polymeric composites with the following composition: PU/HC (100:10, w/w), PU/HC/KEL (100:10:1, w/w), PU/HC/KEL/HA (100:10:1:0.1, w/w), PU/HC/KEL/CS (100:10:1:0.1, w/w), were prepared.

First, PU was dissolved in N, N-dimethylformamide (DMF) to obtain a 30 % (w/w) solution. Then, a suspension of HC in DMF was added into the PU solution at 60^{o}C and stirred for 1 min. In this way composite I was prepared. One quarter of this blend was moved in a capped test tube. The KEL solution was added in the remaining blend, under vigorous stirring, at 45-50^{o}C. After 5-10 min, the mixture became homogeneous and cleared. In this way composite II was prepared and one third was separated in a capped test tube. The remaining blend was divided in two and in each part was added the powder of glycosaminoglycan (HA and CS, respectively), under vigorous stirring at 45-50^{o}C. The four blend variants were poured in glass moulds and dried for 15 h in an air-ventilated drying stove and then under vacuum for 55 h to obtain polymeric composite sheets.

2.3. Preparation of polyurethane film samples

The polyurethane film samples were prepared by solvent casting method. Solvent was evaporated in an oven under circulating air for several hours, and afterwards in a vacuum oven for several days. All these films were used for the research investigations presented in this paper.

2.4. Measurements

Dielectric Relaxation Spectroscopy (DRS) measurements were carried out using a Novocontrol Concept 40 broadband dielectric spectrometer, Germany. Measurements were done at constant temperature by taking frequency scans (1 Hz to 1 MHz) every 5°C between -150 and +100 °C. The temperature was controlled with a 0.1 ºC stability by the Novocontrol Quatro Cryosystem in a dry nitrogen atmosphere. Samples were sandwiched between two gold coated brass electrodes and tested. Samples were around 15 -25 μm thick and had diameters a little larger than that of the upper electrode (20 mm).

Dielectric analysis provides information about the motion of entities having an electric charge in the case of conductivity mechanisms and about the molecules or segments having an electric dipolar moment, in which case information about the dipole reorientations, rotations of the main chain and segmental chains are obtained.

3. Results and discussion

Dielectric data were analyzed in terms of complex dielectric permittivity for dipolar secondary relaxations and electric modulus M^* for charge carriers relaxation and for primary α relaxation.

Dielectric permittivity is expressed as a complex number $\varepsilon^*=\varepsilon'-i\varepsilon''$, where the real part, ε', is the relative permittivity and the imaginary part, ε'', represents the loss factor. The real part is related to the capacitive nature of the material and is a measure of the reversible energy stored in the material by polarization and ε'' is a measure of the energy required for molecular motion, that is the energy dissipated in this motion in the presence of an electric field, divided into relaxation and conductivity contribution (energy required to align dipoles and move ions), [19].

Electric modulus, M^*, represents the reciprocal permittivity, [20]:

$$M^*(f)=1/\varepsilon^*(f)=1/(\varepsilon'-i\varepsilon'') \tag{1}$$

$$M^*(f)=M'(f)+iM''(f)=\frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2}+i\frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2} \tag{2}$$

In electric modulus representation the space charge effects at temperatures above the glass transition are suppressed and an ionic conductivity peak representing conductivity relaxation, σ, is revealed, as seen in Fig. 1 at low frequency and high temperature.

For subglass relaxations, Arrhenius activation maps representing the logarithm of relaxation time as a function of inverse temperature were realized. Relaxation time was obtained for the best fit of dielectric loss vs. temperature at each temperature using WinFit software provided by Novocontrol. For α relaxation, corresponding to glass – rubber transitions, and for free charge relaxation, σ relaxation, relaxation time was determined for M”(T) at several frequencies.

Figs. 1 a and b shows the three-dimensional frequency and temperature dependencies of the dielectric losses, ε'', and electric modulus, M'', for the PU and PU/HC/KEL samples. Dipolar relaxation processes corresponding to thermal transitions are evidenced by loss peaks. For all the samples the representations revealed the same trend as for sample PU. The difference is the temperature at which processes appears, their dependence on temperature and other aspects, like process intensity and shape, discussed in the next paragraphs. A close inspection of Fig.1 shows two secondary partly overlapped relaxations appearing in all the polymers at sub T_g temperatures, designated as γ and β in order of increasing temperature. At higher temperatures appears α relaxation, associated with the dynamic glass transition. At temperatures higher than α relaxation temperature, ε'' increases sharply especially at the lower frequencies, this behavior being attributed to the increasing conductivity: the mobility of the charge carriers increases with increasing temperature. From this reason at lower frequencies the glass transition relaxation is seen as a shoulder.

In electric modulus representation the space charge effects at temperatures above the glass transition are suppressed, α relaxation is better evidenced, and an additional peak representing conductivity relaxation, σ, is revealed, at higher temperatures. On decreasing temperature dipolar relaxations α, β and γ are observed.

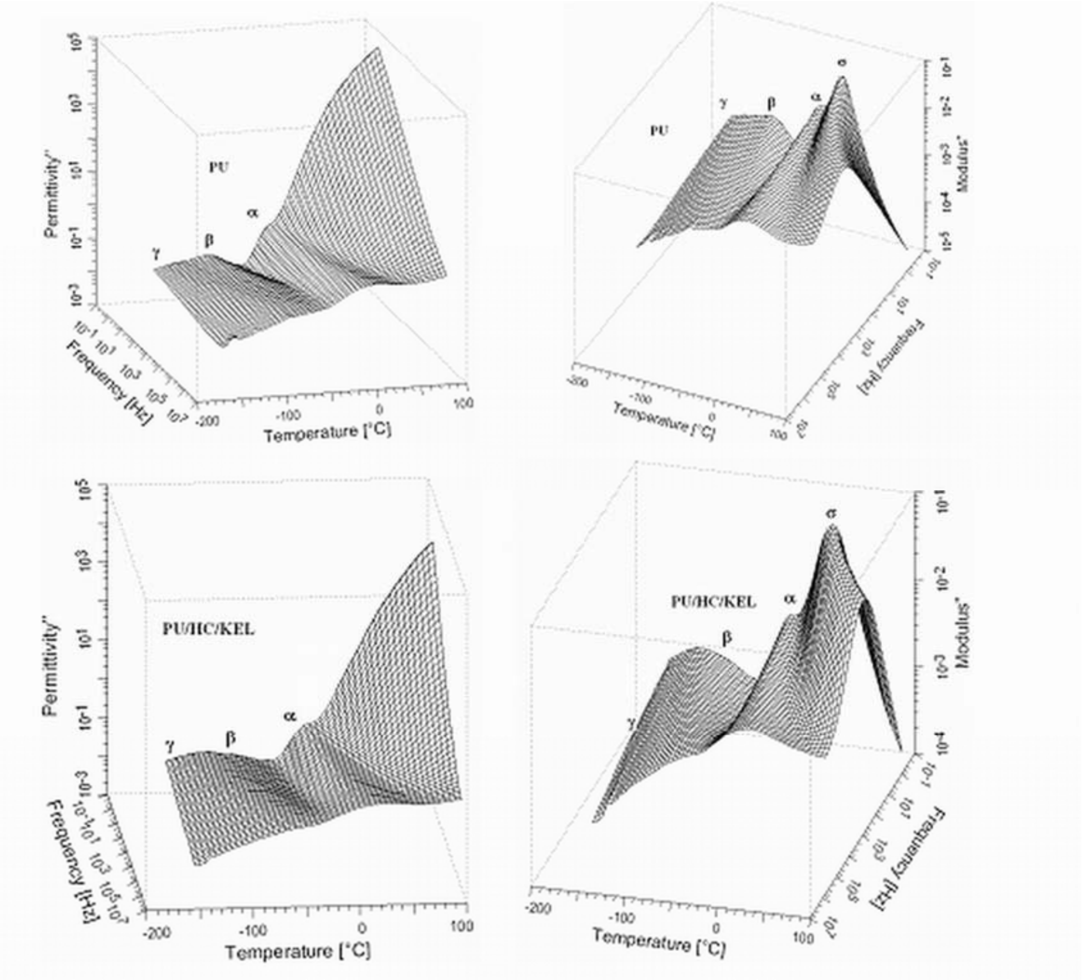


Fig. 1. Frequency and temperature dependencies of the dielectric loss and electric modulus for sample PU and PU/HC/KEL.

Segmental relaxation, which occurs near the glass transition temperature, entails the micro-Brownian motion of several units of a macromolecule. The shape of dielectric dispersion is expected to reflect in some manner the supramolecular structure of polymers. The relatively large values of the activation parameters for this relaxation suggest that large molecular segments are involved. The properties of materials do not depend on the chemical constitution alone, but also on the mutual arrangements and the dynamics of the molecules (supramolecular structure). α relaxation reflects the segmental motion of the chains located in an amorphous phase of polymer. The domain of long-range order which exists in semi- and liquid crystalline systems influences the arrangement of the chains which build the amorphous regions. This result in the appearance of two amorphous fractions in one polymeric system constrained and unconstrained. The co-existence of the amorphous and crystalline phases results in different properties of the amorphous phase.

In order to determine the relaxation parameters, each isothermal dielectric spectrum in -110 ÷-30ºC temperature interval was analyzed by the empirical Havriliak-Negami (HN) function, [21]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{\left[1+\left(i\omega\tau_{HN}\right)^a\right]^b} \qquad (3)$$

where $\Delta\varepsilon=\varepsilon_r - \varepsilon_u$ represent the dielectric strength, ε_r and ε_u represent the relaxed ($\omega\rightarrow 0$) and unrelaxed ($\omega\rightarrow\infty$) values of the dielectric constant for each relaxation, $\omega=2\pi f$ is the angular frequency, a and b represents shape parameters which characterize the width and the asymmetry of the loss curves, and τ_{HN} is the relaxation time for each process and for symmetric relaxation $\tau_{HN} = \tau_{max}=1/2\pi f_{max}$. For secondary relaxation b parameter was found equal to 1, meaning that these relaxations are symmetric, [22].

In Fig. 2 are represented the dielectric loss spectra of all the samples at the temperature of -70 ºC. The two secondary relaxations, β at low frequencies, and γ at high frequencies are evidenced.

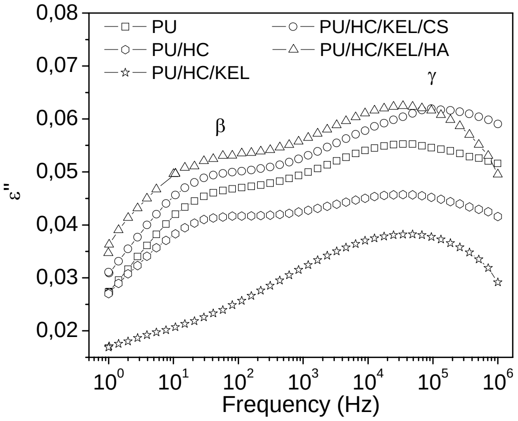


Fig. 2. Dielectric loss spectra ε" as a function of frequency at -70 ºC for all the studied samples.

In Table 1 are presented the fitting parameters for the local relaxation mechanism of the studied samples.

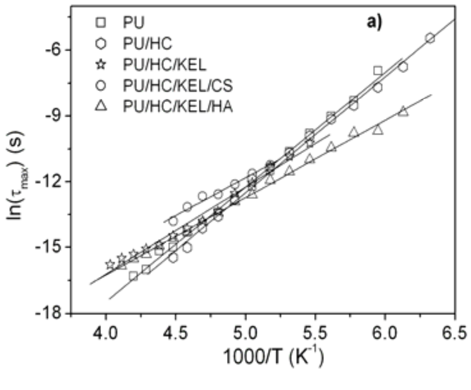
Table 1. Fitting parameters for the local relaxation mechanism of all the samples at -70 ºC.

Sample	*γ* relaxation			*β* relaxation		
	τ_{max} (s)	Δε	a	τ_{max} (s)	Δε	a
PU	2.79×10^{-6}	0.61	0.22	1.14×10^{-2}	0.08	0.54
PU/HC	2.75×10^{-6}	0.56	0.20	1.10×10^{-2}	0.07	0.53
PU/HC/KEL	3.61×10^{-6}	0.22	0.29	9.27×10^{-3}	0.14	0.19
PU/HC/KEL/CS	5.48×10^{-6}	0.40	0.32	1.27×10^{-2}	0.19	0.42
PU/HC/KEL/HA	2.47×10^{-6}	0.49	0.30	1.05×10^{-2}	0.19	0.42

The temperature dependencies of relaxation times were analyzed using an Arrhenius law:

$$\tau(T) = \tau_0 \exp(E_a / kT) \qquad (4)$$

where E_a is the apparent activation energy of the process, k – Boltzmann's constant, τ_0 - the preexponential factor and represents the relaxation time at very high temperature. The temperature dependencies of the relaxation times are shown in the graphs of Figs. 3(a) and 3(b). In Table 2 the corresponding fitting parameters are presented.



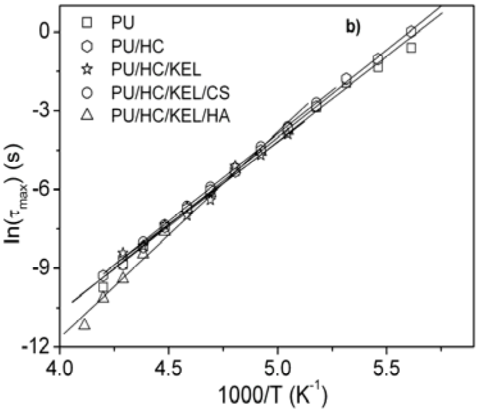


Fig. 3. Arrhenius plots $\ln(\tau_{max})$ vs. 1000/T for the secondary γ (a) and β (b) relaxations for all the samples.

Table 2. Arrhenius parameters for secondary γ and β relaxations mechanisms.

Sample	γ relaxation		β relaxation	
	E_a (kJ/mol)	τ_0 (s)	E_a(kJ/mol)	τ_0 (s)
PU	43.48	2.13×10^{-17}	53.85	1.35×10^{-16}
PU/HC	43.95	1.25×10^{-17}	55.36	6.32×10^{-17}
PU/HC/KEL	33.06	1.12×10^{-14}	51.90	4.22×10^{-16}
PU/HC/KEL/CS	28.73	2.31×10^{-13}	55.39	7.08×10^{-17}
PU/HC/KEL/HA	29.36	6.40×10^{-14}	65.14	2.15×10^{-19}

For linear polyurethanes the secondary (local) γ and β relaxations have been associated with crankshaft motions of the small number of monomeric units in the main chain and with motions of polar carbonyl groups which may have attached water molecules, [23]. Some authors considered that the secondary relaxation β is most probably connected with the local motions of the polar urethane groups, [24, 25].

Activation energies are comparable with other reported values, [26].

Analysis of dielectric spectra in frequency domain *ε”(f)* at constant temperature in *α* relaxation region using HN relation was not possible due to the superposition with conductivity effects. Instead, the relaxation time was calculated as $\tau_{max}=1/2\pi f_{max}$ at temperatures where *M”(T)* corresponds to maximum of *α* peak.

Usually, α-type relaxation process does not fulfill the Arrhenius law. Instead, the Vogel-Fulcher –Tammann-Hesse equation [27] can be applied here:

$$\tau_{max}=A\exp[B/(T-T_0)] \qquad (5)$$

where $\tau_{max}=1/2\pi f_{max}$, f_{max} – the frequency of maximal value of *M”(T)*, *A* and *B* are constants, *T* – the temperature in K and T_0 – the extrapolated (Vogel) glass temperature. At T_0 the fractional free volume becomes zero and the molecular movement vanishes. An apparent, temperature dependent activation energy can be calculated formally from eq. (5), this value is proportional with the slope *B* [27]. The values obtained by best fitting of relaxation times with eq. (5) are listed in Table 3.

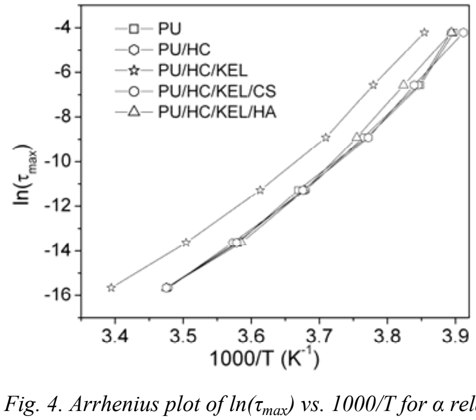


Fig. 4. Arrhenius plot of ln(τ_{max}) vs. 1000/T for α relaxation.

Table 3. Vogel-Fulcher-Tammann-Hesse equation fitting parameters.

Sample	A	B	T_0 (K)
PU	29.75	1.21	212
PU/HC	34.85	1.64	202
PU/HC/KEL	32.82	1.50	207
PU/HC/KEL/CS	30.75	1.10	215
PU/HC/KEL/HA	34.54	1.51	207

The different values of fitting parameters of Vogel-Fulcher-Tammann-Hesse equation corresponding to different matrix compositions, with added of small amounts of extracellular matrix components, can be related to changes in hydrogen bonding distribution in the supramolecular architecture of the resulted biocomposites.

4. Conclusions

The molecular motions for polyurethane biocomposites were investigated by use of dielectric spectroscopy as function of temperature and frequency. The presence of hydrogen bonding in the supramolecular structure of biocomposites is correlated with conductivity, relaxation transitions and activation energy. This study is very important for biomaterials because their electrical properties and dynamic heterogeneity exert major influence on protein adsorption from sanguine plasma and conformation. The dielectric properties are needed for purposes such as the development of telemetry or diagnostic applications. They also can provide useful information about the structure and function of tissues.

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*Corresponding author: eradro2002@yahoo.com