DESCRIPTION OF DIELECTRIC SPECTRUM OBTAINED BY DIELECTRIC RELAXATION SPECTROSCOPY USING HAVRILIAK – NEGAMI FUNCTION

Inas Abuetwirat

Doctoral Degree Program (3), FEEC BUT

E-mail: xabuet00@stud.feec.vutbr.cz

Supervised by: Karel Liedermann

E-mail: Liederm@feec.vutbr.cz

Abstract: Solids exhibit a distribution of relaxation times, because there are always some nonuniformities in local domains, which will alter a response of individual dipoles or charges in dielectric materials. Havriliak – Negami (HN) equation is the most frequently used function for the description of the properties of dielectric materials in frequency domain. The main aim of this paper is to find the parameters of the HN function by graphically analyze the real and complex permittivity of the Cole-Cole plot as proposed by HN function, and shows the deviation of the measurements from calculated value.

Keywords: Havriliak Negami (HN) equation, fitting theoretical function to experimental data, finding the parameters of HN function

1. INTRODUCTION

Dielectric spectroscopy is an experimental tool which enables to establish significant information about dielectric properties of matter. In the dielectric relaxation region, relative permittivity in frequency domain describes the interaction of electromagnetic wave parameters of observed phenomenon (relaxation time, conductivity, dielectric increment etc) [1]. The analysis of measured complex permittivity is usually performed by a curve-fitting technique based on one of the following models: Debye model, Cole – Cole model, Davidson – Cole model, Havriliak – Negami (HN) model and Kohlrausch – Williams – Watts (KWW) model. The curve fitting analysis is typically used to find the relaxation time and other dielectric parameters by graphically analyzing the Cole-Cole plot proposed by the HN function. This is the aim of this paper.

2. THEORETICAL PART

The description of dielectric relaxation in terms of the HN empirical equation for complex permittivity ε^* has been shown to be of great use in dealing with polymeric materials [2].

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

where ε_0 is the limited low-frequency (static) permitivity, ε_∞ is the high–frequency dielectric constant , τ_0 is the central relaxation time, and b and c are shape parameters ranging between 0 and 1, which describe the symmetric or asymmetric broadening of the relaxation time distribution function, respectively. Or in other words, b represents the width and c represents the skewness of the dielectric loss $\varepsilon''(\omega)$ when viewed in log (ω) plot. The HN relaxation function which is a frequency-domain function is then used to obtain the complete spectra of dynamic properties of the specific material.

The real and imaginary part of permittivity can be derived from equation (1) as follows [3]

$$\varepsilon' = (\varepsilon_0 - \varepsilon_\infty) r^{-c} \cos(\omega\psi) + \varepsilon_\infty \tag{2}$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) r^{-c} \sin(c\psi) \tag{3}$$

with

$$r^2 = 1 + 2(\omega\tau_0)^b \cos(b\pi/2) + (\omega\tau_0)^{2b} \tag{4}$$

and

$$\tan\psi = \frac{(\omega\tau_0)^b \sin(b\pi/2)}{1 + (\omega\tau_0)^b \cos(b\pi/2)} \tag{5}$$

With $\omega\tau_0$ going towards infinity, ε' (ω) reaches ε_∞ and ε'' (ω) reaches zero. In addition, with $\omega\tau_0$ going towards zero, ε'(ω) reaches ε_0 and ε''(ω) reaches 0 for this reasons, two of the dispersion parameters ε_0 and ε_∞ can be evaluated as high-frequency and low-frequency intercepts of the experimental ε'(ω) with the real axis of Cole –Cole plot [4].

The relaxation process can be expressed in terms of a relaxation time spectrum (the distribution of relaxation processes, each with a different time constant) by the following equation [5]

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_{-\infty}^{\infty} \frac{F(\tau/\tau_0)}{1 + i\omega\tau} d\, In(\tau/\tau_0) \tag{6}$$

The associated relaxation time spectrum is given by

$$F(\tau/\tau_0) = \frac{(\tau/\tau_0)^{bc} \sin(c\theta)}{\pi\left[(\tau/\tau_0)^{2b} + 2(\tau/\tau_0)^b \cos(\pi b) + 1\right]^{c/2}} \tag{7}$$

where

$$\theta = \arctan\left|\frac{\sin(\pi b)}{(\tau/\tau_0)^b + \cos(\pi b)}\right| \tag{8}$$

In case of two different processes α (which corresponds to the peak occurring at the highest temperature) [4], and β (is the peak at a lower temperature), the permittivity reads

$$\varepsilon^* = (\Delta\varepsilon^*)_\alpha + (\Delta\varepsilon^*)_\beta + (\varepsilon_\infty)_\beta \tag{9}$$

By considering that $\Delta\varepsilon_\alpha = \varepsilon_{0\alpha} - \varepsilon_\alpha$ and $\Delta\varepsilon_{0\beta} = \varepsilon_{0\beta} - \varepsilon_\beta$ one obtains

$$\Delta\varepsilon^*_\alpha = \int_{-\infty}^{\infty} \Delta\varepsilon_\alpha \frac{F(\tau/\tau_{0\alpha})}{1 + i\omega\tau_\alpha} d\ln(\tau/\tau_{0\alpha}) \tag{10}$$

and

$$\Delta\varepsilon^*_\beta = \int_{-\infty}^{\infty} \Delta\varepsilon_\beta \frac{F(\tau/\tau_{0\beta})}{1 + i\omega\tau_\beta} d\ln(\tau/\tau_{0\beta}) \tag{11}$$

By substituting equations (10) and (11) into equation (9) we obtain the complete relaxation process

$$\frac{\varepsilon^* - \varepsilon_{\infty\beta}}{\varepsilon_{0\alpha} - \varepsilon_{\infty\beta}} = \int_{-\infty}^{\infty} \frac{F_{\alpha+\beta}(\tau/\tau_{0\alpha})}{1 + i\omega\tau_\alpha} d\ln(\tau/\tau_{0\alpha}) \tag{12}$$

with

$$F_{\alpha+\beta}(\tau/\tau_{0\alpha}) = \frac{\Delta\varepsilon_\alpha}{\varepsilon_{0\alpha} - \varepsilon_{\infty\beta}} F_\alpha(\tau/\tau_{0\alpha}) + \frac{\Delta\varepsilon_\beta}{\varepsilon_{0\alpha} - \varepsilon_{\infty\beta}} F(\tau/\tau_{0\beta}) \quad (13)$$

by considering that d(ln ($\tau/\tau_{0\alpha}$)) = d(ln ($\tau/\tau_{0\beta}$)).

3. MEASUREMENTS

To analyze the measured dielectric function, we plotted the real part of complex permittivity in the x-axis and the imaginary part in the y-axis. This is known as the Cole-Cole plot. Fitting the measured data to equation (1) in case of a single relaxation peak allows to find the five-parameter HN function. The inter section with ε'–axis at high frequency is the ε_∞ and the inter section with ε'–axis at low frequency is ε_0. An example of the result that might be achieved by fitting the data to the equation (1) as adopted from [5] is shown in Fig. 1 for one single relaxation peak.

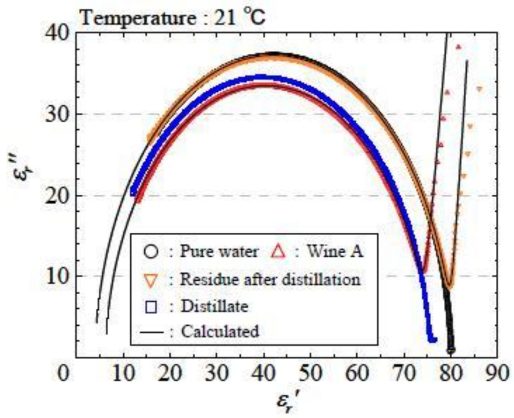

Figure 1: Cole-Cole plots measured for red wine, its distillate and residue and calculating fitting [5].

Table 1 obtained from the fitting data of red wine to equation (1) adapted from [5].

Merlot wine	ε_0	ε_∞	b	τ_0	f_m[MHz]	c
Wine A [2006]	73.6 (12.2)	6.2	0.986	12.76	789	0.910
Residue	79.5	4.0	0.986	9.64	898	0.930
Distillate	75.5<12.1>	4.9	0.983	12.61		

Table 1: (HN) parameters obtained from the fitting data of red wine to the equation 1.

In case of two different process α and β as shown below it was adopted from [3] it is estimates the HN parameters by fitting the measured data to equations (1) and (9) as the following

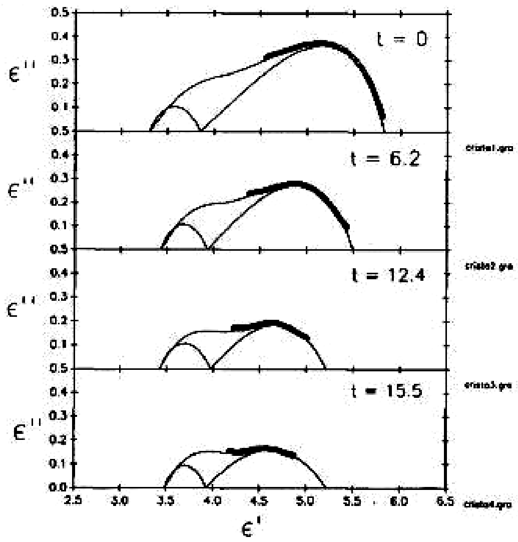

Figure 2: Cole-Cole plots for selected crystallization times at $T_c = 110C^0$.solid curve denote calculated values according to equation 1 adopted from [3].

Table 2 obtained from the fitting data of poly (ethylene terephthalate) to equation (1) adopted from [3].

τ_0	$\Delta\varepsilon_\alpha$	b_α	c_α	$(\tau_0)_\alpha$	$\Delta\varepsilon_\beta$	b_β	$(\tau_0)_\beta$
0	1.97	0.74	0.30	8.83×10^{-6}	0.55	0.46	1.89×10^{-9}
6.2	1.56	0.61	0.41	1.05×10^{-5}	0.51	0.51	2.7×10^{-9}
12.4	1.24	0.45	0.57	2.29×10^{-5}	0.55	0.47	2.5×10^{-9}
15.5	1.29	0.34	0.75	2.46×10^{-5}	0.45	0.51	4.6×10^{-9}

Table 2: $\Delta\varepsilon_\alpha$ b_α c_α and $(\tau_0)_\alpha$ obtained from the fitting of equation 1.the extrapolated parameters corresponding to the β process are denoted by $\Delta\varepsilon_{\beta,}$ b_β and $(\tau_0)_\beta$ adopted from [3].

4. CONCLUSIONS

The dielectric relaxation response is generally analyzed in terms of the HN relaxation function which is a frequency-domain function. The HN function is then used to obtain complete spectra of dynamic properties of a specific dielectric material at a given temperature. Fitting HN theoretical function to experimental data gives the values of five empirical parameters ε_∞, ε_0, τ_0, b and c, which can be subjected to a more detailed analysis of the relaxation.

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