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Moisture absorption is a water diffusion process known to alter many of the mechanical properties of polymers and polymer-based composites. Ultrasonic waves are sensitive to such changes of properties and allow *in situ* measurements to be performed. This paper presents linear and nonlinear ultrasonic measurements on 12 phenolic resin plates with water contents ranging from 0% to 5% of their dry mass. Linear parameters are evaluated by an insertion/substitution spectroscopy method yielding to a representation of the evolution, with frequency, of the attenuation and of the phase velocity of acoustic waves propagating in each sample. Nonlinear β coefficient of each sample is determined by a contact phase modulation method. The evolution, with moisture content, of acoustic parameters such as the attenuation and the phase velocity of acoustic waves propagating at a given frequency, the slope of their attenuation with frequency, and the β coefficient of each sample is then studied. Results are discussed in terms of sensitivity. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356787]

I. INTRODUCTION

In industrial applications, materials can be submitted to various environmental conditions such as x rays or γ rays, temperature variations, and light or mechanical loadings. Among those, moisture has a great influence on polymers and polymer-based composites due to their capability to absorb water. One of the major consequences is a shift of the glass transition temperature.[1] The appearance of microcracks due to induced residual stresses has also been observed.[2] In phenolic resins, the moisture content can reach 5% of the dry mass inducing swelling and density variations.[3,4] Nuclear magnetic resonance spectroscopy[5] or weight measurements are the most commonly used characterization methods, but they are generally destructive.

Because of the change of the material mechanical properties, moisture content can be estimated using acoustic waves. The method is nondestructive and allows *in situ* measurements. The sensitivity of Lamb waves to the moisture content of composite samples has recently been investigated.[6] Bulk wave velocity measurements have also been performed to characterize the water content in concrete.[7]

In the present work, we report measurements of linear and nonlinear acoustic properties of phenolic resins with carefully controlled water contents. According to the authors, no study was carried out on as many calibrated samples by acoustic measurements. First, linear parameters such as acoustic wave velocities and attenuations are identified using a through transmission ultrasonic spectroscopy technique. A contact phase modulation method was then adapted to evaluate the longitudinal nonlinear parameter of each sample. The results are discussed to determine the most sensitive parameters to moisture content and the corresponding evaluation methods.

II. MATERIAL CONDITIONING

A. Moisture content in polymer samples

Diffusion is the process of water transport in a medium. In isotropic or anisotropic materials, a simple model is given by the Fick law,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \tag{1}$$

where C is the water concentration, D is the water diffusion coefficient of the considered material, and x is the diffusion axis. In the following, the studied samples are resins commonly supposed to be isotropic. The moisture content is defined by

$$U = \frac{m - m_0}{m_0} \times 100, \tag{2}$$

where m_0 is the sample dry mass and m is the sample mass variable during the diffusion process. The amount of moisture in any given material is a function of its environment's relative humidity (RH) determined for the water content equilibrium state. The absorbed water mass at the equilibrium (m_∞) can be described by[1]

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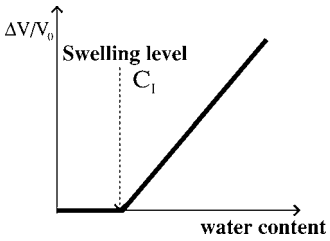

FIG. 1. Swelling of a polymer vs water content.

$$m_\infty = a(\mathrm{RH})^b, \tag{3}$$

where a and b are material constants.

Swelling curves are used to describe the volumetric changes of a material due to the moisture absorption at a given temperature. To understand the swelling phenomenon, Adamson[3] considers the free volume equal to the difference between the effective polymer volume and the volume really occupied by the actual mass. It corresponds to the cavities or voids in the sample. During the first part of the diffusion process, this free volume is filled by water. The water content thus increases without swelling (Fig. 1). At water content C_1, the free volume is filled and further water absorption induces displacements of macromolecule chains. The sample volume is then increased. In each part of the process, water absorption is accompanied by a change of the sample density.

B. Conditioning

For this work, twelve 35×35 mm^2 and 3 mm thick phenolic resin samples have been manufactured. They have been dried and then kept under seven various hygrometric conditions. In the following, the mass in the dried condition is chosen as a reference. The various relative environmental humidities are 0%, 22%, 33%, 44%, 55%, 76%, and 100%. The RH and the water content of each sample are presented in Table I. The 100% RH corresponds to immersed samples. For 0% RH, samples are kept under vacuum. Water content in sample 3 is negative because it was not totally dry before being conditioned. The other samples are conditioned in desiccators that contain a mixture of water and salt, ensuring a fixed hygrometry of salt saturated vapor. The samples are kept under these conditions in order to stay at the equilibrium state m_∞. In this work, m_∞ and m are assumed to be equivalent meaning that there is no moisture gradient across the sample thickness.

TABLE I. Samples of phenolic resin, relative humidity (RH) environment, and corresponding water content.

Sample No.	RH (%)	Water content (%)	Sample No.	RH (%)	Water content (%)
1	0	0	7	44	1.8063
2	0	−0.0685	8	55	2.2153
3	22	0.9455	9	55	2.0784
4	33	1.4972	10	76	3.1403
5	33	1.5675	11	100	4.3222
6	44	1.7428	12	100	4.2593

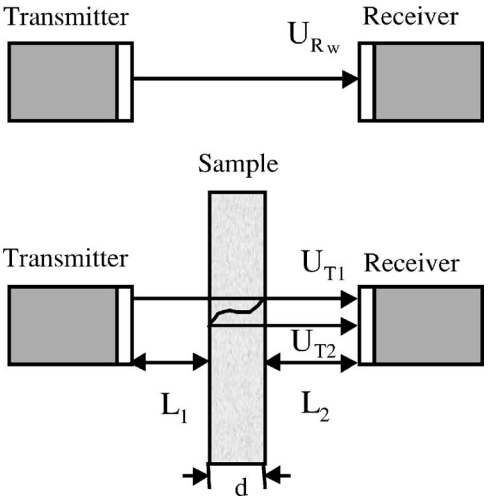

FIG. 2. Principle of pulse spectroscopy for attenuation and phase velocity determination.

In this study, we assume that the densities of the samples are constant. Indeed, the phenolic resin and water densities are very close, and the amount of absorbed water is quite low. Density measurements have been performed using Archimedes principle. The phenolic resin sample density is found equal to 1.26 ± 0.01 g cm^{-3}.

III. ACOUSTIC MEASUREMENTS

In this section, measurements are performed to evaluate acoustic parameters of samples with different moisture contents. Due to the low amounts of water in the samples, high precision measurement methods are required. To measure linear parameters, the insertion/substitution spectroscopy method[8] was chosen. Indeed, to obtain a reproductible coupling between transducers and the samples, the plates were immersed in water. The properties of the reference medium are then well known and acoustic measurements allow to identify each sample thickness with a high precision.

Several methods, such as the identification of the second harmonic component[9–11] or the measurement of acoustic-radiation stress,[12] can be developed to characterize the nonlinear parameter β in solids. Parametric interactions[13] or shock waves[14] have also been used. They allow an indirect measurement of the third order elastic constants. In this work, a parametric interaction method in the form of a contact phase modulation is chosen. Indeed, it allows to get rid of the nonlinear effects of the measurement chain. Moreover, this method is also well adapted to homogeneous media.

A. Linear parameter determination

Figure 2 presents the insertion/substitution spectroscopy principle used to determine the phase velocity and the attenuation of the acoustic waves propagating in the samples. Two transducers with central frequency equal to 3.5 MHz are set facing each other in water. First, a measurement of a broadband signal U_{R_w} transmitted through the reference medium (water) is done (upper case in Fig. 2). The sample is then inserted between the two transducers (lower case in Fig. 2). Because it is oriented perpendicular to the transducers' axis,

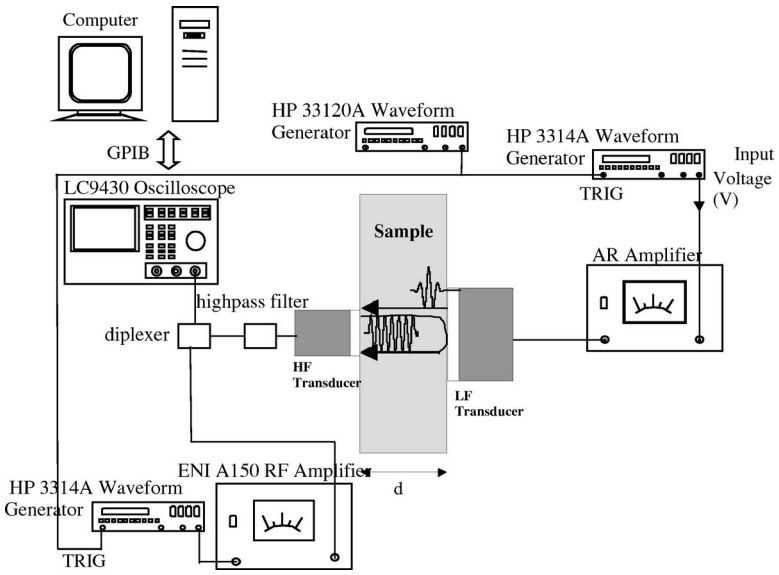

FIG. 3. Experimental setup for phase modulation measurement.

several reflections appear in the thickness of the sample. The direct and second transmitted pulses U_{T1} and U_{T2} are then measured and all received signals are digitized using a numerical oscilloscope. They are then acquired via general purpose interface bus (GPIB) on a personal computer (PC) for further processing. The hydrometric equilibrium state of the samples is ensured because of the measurement process rapidity (less than a few minutes) compared to the kinetics of water diffusion in the resin.

The longitudinal wave phase velocity in the sample, as a function of the angular frequency ω, is given by

$$c = c_w\left(1 - \frac{2\Delta\phi}{\Delta\phi_{12}}\right), \tag{4}$$

where c_w is the phase velocity in water, $\Delta\phi$ the phase delay between U_{R_w} and U_{T1}, and $\Delta\phi_{12}$ the phase delay between U_{T1} and U_{T2}. The wave attenuation in the sample, as a function of the angular frequency, is given by

$$\alpha = -\frac{\omega}{c_w[\Delta\phi - (\Delta\phi_{12}/2)]}\ln\left(\frac{A}{T^2}\right), \tag{5}$$

where A is the ratio of U_{T1} and U_{R_w} the spectrum magnitudes. T^2 is defined by

$$T^2 = T_{sw}T_{ws}, \tag{6}$$

where $T_{sw}=2Z/(Z+Z_w)$ and $T_{ws}=2Z_w/(Z_w+Z)$ are, respectively, the transmission coefficients at the sample-water and water-sample interfaces. $Z=\rho c$ and $Z_w=\rho_w c_w$ are the acoustic impedances of sample and of the water. ρ and ρ_w are the sample and water densities, respectively. One can notice that, through $\Delta\phi$ and $\Delta\phi_{12}$, the thickness of sample is involved in all these calculations.

B. Nonlinear parameter measurement: Phase modulation method

The contact method used to measure the nonlinear coefficient β is the one described in Ref. 15. This method is based on the interaction between a low frequency acoustic wave and a high frequency one.[16] The typical frequency ratio is 1/10. The low frequency wave creates a phase modulation of the high frequency signal expressed by[17]

$$\Delta\phi = \frac{\omega_{\mathrm{HF}}d}{c^2}\beta\nu_{\mathrm{LF}}e^{\alpha d}, \tag{7}$$

where ν_{LF} is the particle velocity of the low frequency wave at the transducer surface, α is the attenuation of the low frequency wave, ω_{HF} is the angular frequency of the high frequency wave, d is the thickness of the sample, and c the phase velocity in the sample. Finally, the nonlinear coefficient β in solids is defined by

$$\beta = -\left(\frac{3}{2} + \frac{C_{111}}{2C_{11}}\right), \tag{8}$$

where C_{11} and C_{111} are the second and third order longitudinal elastic moduli.

The experimental setup allowing to perform phase modulation measurements is shown in Fig. 3. A 0.25 in. diameter Panametrics planar contact transducer is driven by a 15 MHz sinusoidal tone burst of ten periods. The signal is delivered, through a 55 dB ENI A 150 power amplifier, by an HP 3314A wave form generator. The high frequency (HF) wave has to be amplified because of the high attenuation in phenolic resin. After propagation through the sample, the wave is reflected at the opposite face. Simultaneously, a Panametrics low frequency (LF) contact transducer emits a 2.63 MHz pulse generated by an HP 3314A and 55 dB amplified by an AR power amplifier. The two HP3314A generators are triggered by the same HP 33120A wave form generator, so that the reflected HF acoustic wave interacts with the LF pulse during its back propagation. The received signal is recorded by a LeCroy 9430 digital oscilloscope and transmitted to a computer via a GPIB bus. In order to increase the signal to noise ratio, a 1000 sweep averaging is performed. Finally, the phase modulation of the HF received signal, produced by the nonlinear interaction in the sample, is numerically evaluated.

TABLE II. Table of linear and nonlinear results.

Sample No.	α (Np/m)	Slope of α (Np/m/MHz)	c (m/s)	C_{11} (GPa)	β	C_{111} (GPa)
1	83	7.01	2970	11.1	7.2	−190
2	89	6.8	2963	11.0	6.8	−180
3	115	11.6	2970	11.1	8.4	−220
4	121	16	2947	10.9	9.7	−240
5	123	18.4	2953	10.9	10.5	−264
6	127	18.5	2935	10.8	12.9	−310
7	128	17.1	2953	10.9	11.8	−290
8	133	21	2923	10.7	13.4	−320
9	137	21.4	2917	10.7	13.5	−320
10	143	26.3	2879	10.4	14	−323
11	142	28.7	2797	9.8	13.3	−290
12	141	29.7	2795	9.8	13.5	−290

C. Results

Linear measurements were performed in a way to identify the wave velocity from Eq. (4) and its attenuation from Eq. (5). Table II summarizes the wave velocity and the attenuation measured, in each sample, at 2.63 MHz. Moreover, it presents the slope of the attenuation studied in the large frequency spectrum of the excitation. The nonlinear coefficient β of each sample is also presented in the table as well as its second and third order elastic moduli, deduced from the density, the velocity, and the nonlinear coefficient.

1. Linear measurements

Figure 4 presents the evolution, between 2 and 5 MHz, of the phase velocity measured in each sample. For a given plate, a slight dispersion of approximately 20 m s^{-1} is observed across the transducer bandwidth. The phase velocity clearly appears as being linked to the moisture content, except for very low values. In a similar way, the evolution, between 2 and 5 MHz, of the attenuation, measured in each plate, is presented in Fig. 5, showing a monotonous dependence with the frequency. Both the attenuations (α) and their slopes with frequency depend on the moisture content.

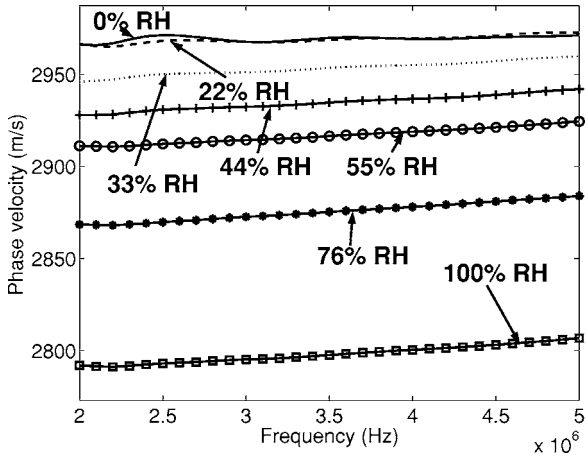

FIG. 4. Phase velocity vs frequency for different moisture contents in phenolic resin samples.

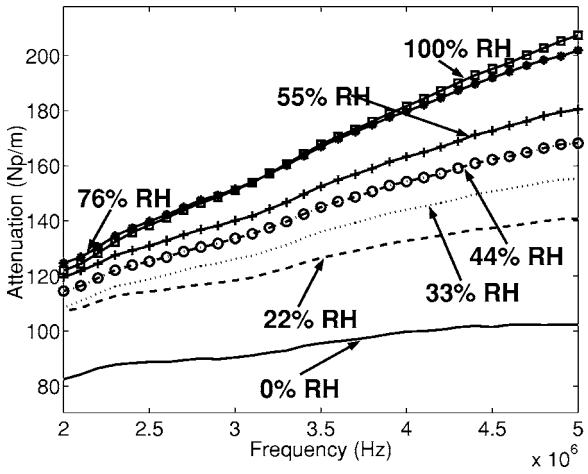

FIG. 5. Parametric evolution of the attenuation vs frequency for various moisture contents in phenolic resin samples.

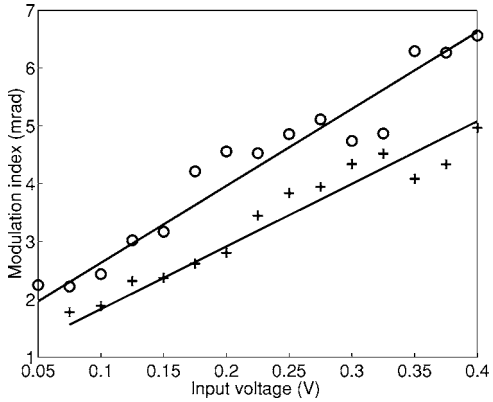

FIG. 6. Modulation index for samples 6 (cross marker) and 21 (circle marker) as a function of the input level voltages of the low frequency generator.

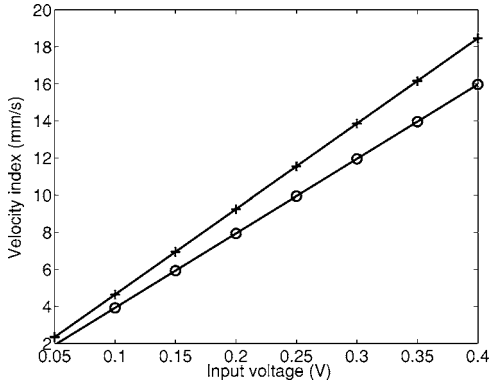

FIG. 7. Velocity index for samples 6 (cross marker) and 21 (circle marker) as a function of the input level voltages of the low frequency generator.

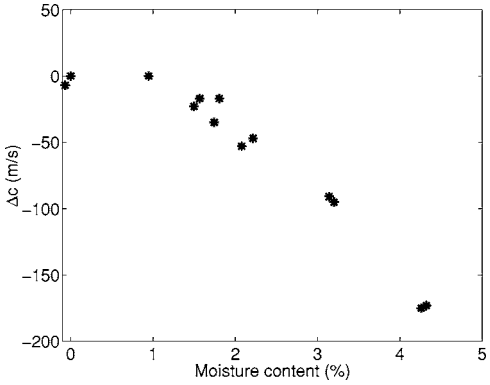

FIG. 8. Relative phase velocity Δc vs moisture content in phenolic resin at 3.5 MHz.

2. Nonlinear measurements

The nonlinear coefficient can be deduced by inverting Eq. (7). Figures 6 and 7 present the phase modulation and the velocity indices of samples 6 and 21. These parameters correspond to the difference between the maximum and the minimum of the phase modulations and velocities measured, in the samples, for different excitation levels. Two linear fits are then performed to extract $\Delta\phi$ and ν_{LF}, yielding to the identification of the ratio $\Delta\phi/\nu_{\mathrm{LF}}$. As already mentioned, the second elastic moduli of the samples can be deduced from the density and the velocity. Considering the density constant for all of the samples, the evolution, with the moisture contents, of the second order elastic moduli is very close to that of the phase velocity. The third order elastic constants can be obtained from C_{11} and β. It shows a good sensitivity to the moisture content, in particular, in the 1.5%–2% range.

D. Discussions

Figure 8 presents the evolution, with the moisture content, of the difference between the phase velocity measured at 2.63 MHz in each sample and that measured in the dry sample 2. The velocity remains constant up to 1% of water content and then decreases. This trend can be explained by the free volume concept. During the first stage, the sample does not swell because the water fills in the vacancies in the sample. This should lead to an increase of the stiffness of the material, leading to a velocity increase. However, this cannot be observed here, due to the lack of data for moisture contents from 0% to 1%. In a second stage, the water mixes with the phenolic resin and generates swelling. The fact that the phase velocity is lower in water than in the resin explains the observed decrease of the velocity with water content.

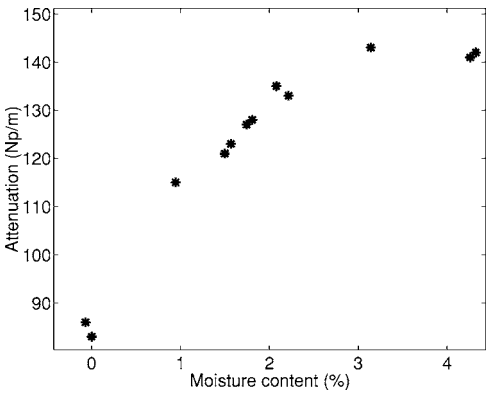

FIG. 9. Attenuation vs moisture content in phenolic resin samples at 2.63 MHz.

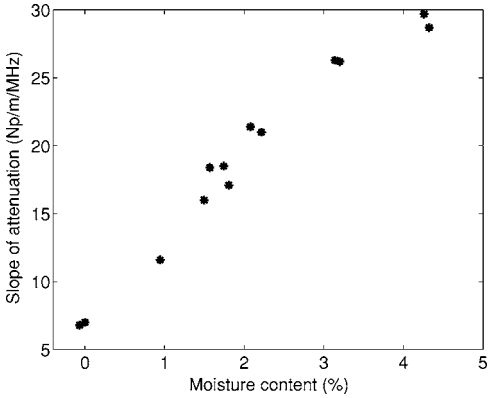

FIG. 10. Slope of attenuation (Np/m/MHz) vs moisture content in phenolic resin.

Figure 9 presents the evolution of the attenuation measured, at 2.63 MHz, in each sample. The attenuation is found to be twice higher in samples having an increase of 4.3% in mass than in the dry ones. A significant increase, fairly linear with moisture content ranging from 0% to 3%, can be observed. Then, the attenuation remains constant up to 4.3%. This plateau is a major drawback for moisture content identification with attenuation measurements. Another disadvantage is due to the fact that the measured attenuations are very sensitive to a defect in the flatness of the sample surfaces.

Figure 10 presents the slope with frequency of the attenuation, as a function of moisture content. This parameter is commonly used in medical acoustics[18] and referred to as broadband ultrasonic attenuation (BUA). It shows a great sensitivity to the water content since it increases with a factor 4 in the investigated range. This parameter is suitable for all moisture content rates and has the advantage of being much less sensitive to experimental condition variations than the attenuation values themselves.

The evolution, with the moisture content, of the nonlinear parameter β is shown in Fig. 11. First, it increases moderately. Then, a sharp variation, from 1.5% to 2%, is observed. Finally, it remains constant for moisture contents

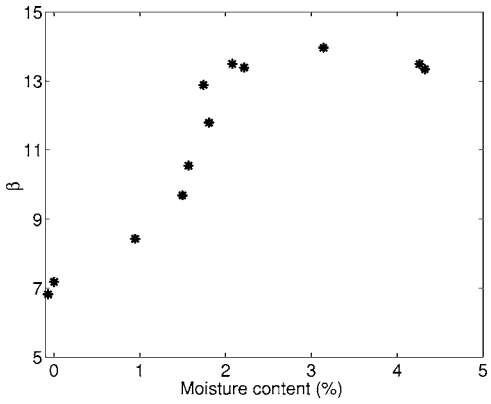

FIG. 11. Nonlinear parameter β vs moisture content in phenolic resin.

higher than 2%. The evolution of β can be explained from the evolution of the phase velocity. Indeed, when the phase velocity increases, the sample can be seen as stiffer and the nonlinear effects take place for higher excitation amplitudes. Consequently, the nonlinear parameter should decrease. On the contrary, when the phase velocity decreases, the nonlinear parameter should increase. In the case of a liquid mixture (water and ethanol), a slight decrease of the nonlinear parameter with the concentration of one element of the mixture was found by Sehgal *et al.*[19] and Jacob.[20] One can expect the same evolution here but more measurement points would be needed in the 0%–1% range. Unfortunately, it is very delicate to maintain samples at such relative humidities.

IV. CONCLUSION

Linear and nonlinear acoustic parameters (velocity, attenuation, and β coefficient) have been measured on phenolic resin plate samples with various moisture contents in the range of 0%–4.3% of the dry mass. These measured parameters reveal important differences in terms of sensitivity and show different evolution regimes according to moisture content ranges. Attenuation curves present a monotonous increase followed by a plateau. As a consequence, this parameter is only suitable to identify small percentages of water content. The phase velocity is nonmonotonous, since little variations are observed at low values of moisture contents and then a linear decrease is found. This disadvantage is compensated by the fact that the study of this parameter reveals valuable information on the physics of water absorption. The nonlinear coefficient β is also nonmonotonous and seems to be sensitive to moisture content only in the middle range, i.e., between 1.5% and 2% of the dry mass. Finally, the slope of the attenuation with the frequency is found to be monotonous, on the entire studied range of moisture contents. This characteristic indicates that this parameter appears as the most promising tool to nondestructively measure or monitor moisture content in polymer or polymer-based materials.

ACKNOWLEDGMENT

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[1] E. L. McKague, J. D. Reynolds, and J. E. Halkias, J. Appl. Polym. Sci. **22**, 1643 (1978).
[2] B. Dewimille and A. R. Bunsell, J. Phys. D **15**(10), 2079 (1982).
[3] M. J. Adamson, J. Mater. Sci. **15**, 1736 (1980).
[4] V. B. Gupta and L. T. Drzal, J. Appl. Polym. Sci. **30**, 4467 (1985).
[5] D. Le Botlan, Y. Rugraff, C. Martin, and P. Colonna, Carbohydr. Res. **308**, 29 (1998).
[6] M. Cinquin, M. Castaings, B. Hosten, P. Brassier, and P. Pérès, NDT & E Int. **38**, 37 (2005).
[7] E. Ohdaira and N. Masuzawa, Ultrasonics **38**, 546 (2000).
[8] P. He, J. Acoust. Soc. Am. **107**, 801 (1999).
[9] M. A. Breazeale and J. Ford, J. Appl. Phys. **36**, 3486 (1965).
[10] G. E. Dace, R. B. Thompson, O. Buck, Rev. Prog. Quant. Nondestr. Eval. **11**, 1685 (1991).
[11] R. B. Thompson, O. Buck, and D. O. Thompson, J. Acoust. Soc. Am. **59**, 1087 (1976).
[12] W. T. Yost and J. H. Cantrell, Phys. Rev. B **30**, 3221 (1984).
[13] J. Y. Duquesne and D. A. Parshin, J. Appl. Phys. **82**, 3275 (1997).
[14] R. A. Graham, J. Acoust. Soc. Am. **51**, 1576 (1972).
[15] M. Vila, F. Vander Meulen, S. Dos Santos, L. Haumesser, and O. Bou Matar, Ultrasonics **42**, 1061 (2004).
[16] V. A. Zverev and I. A. Kalachev, Sov. Phys. Acoust. **16**, 204 (1971).
[17] C. Barriere and D. Royer, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **48**, 1706 (2001).
[18] R. Strelitzki and J. G. Truscott, Med. Eng. Phys. **20**, 132 (1998).
[19] M. C. Sehgal, R. B. Porter, and F. J. Greenleaf, J. Acoust. Soc. Am. **79**, 566 (1986).
[20] X. Jacob, Ph.D. thesis, Université Paris VII-Denis Diderot, 2005.