Determination of the viscoelastic shear modulus of poly(isobutylene)/solvent systems using thickness-shear mode quartz resonators

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Abstract

Determination of the storage modulus, G', loss modulus, G'', and, consequently, the shear moduli, G ($G = G' + jG''$), of polymer and polymer/solvent systems was conducted in this study using a thickness-shear mode (TSM) quartz resonator. The polymer poly(isobutylene) was spin-coated as a film of a few microns thickness on the surface of the TSM device and, upon inducing oscillation of the device at its resonance frequency (several mega-Hertz), the impedance characteristics were measured. In addition, the poly(isobutylene) was exposed to known weight concentrations, up to 20%, of benzene, toluene, cyclohexane, hexane, dichloromethane, and chloroform vapors diluted in nitrogen gas, and the impedance characteristics were measured. These data sets collected from the impedance analyzer were then examined by modeling the polymer and polymer/solvent loaded TSM device with an electrical equivalent circuit model to yield the shear moduli, which enters as a parameter in the mathematical theory describing this circuit model. In the work done thus far, the shear modulus for pure poly(isobutylene) as a function of temperature has been determined and compared to previously obtained data[11]. Good agreement with the trend of our results and the literature demonstrates that the experimental apparatus and equivalent circuit modeling is valid.

Introduction

The use of viscoelastic films as sensing layers implemented in chemical and biological sensor technology is greatly established; however, limitations exist in their application due to the lack of data characterizing the film deposited on the sensor platform in its pure state and in contact with various external factors such as solvent vapor exposure. Reported in this work are the storage and loss moduli of poly(isobutylene) exposed to six solvents in the vapor phase at 298.15 K and ambient overall pressure. To measure the data, a TSM resonator was utilized over other viable techniques because of its rapid response and high sensitivity to mass loading, simplicity in application, and supporting of shear horizontal waves. Utilizing shear horizontal waves significantly eases the extraction of the shear modulus[1].

In extracting the shear modulus reliably, it is essential that the film thickness is such that the film exhibits viscoelastic tendencies. Viscoelastic effects are primarily responsible for significant changes in the motional resistance of the circuit as the film thickness increases up to a certain point depending on the particular viscoelastic film. Constancy in resistance

beyond this threshold thickness signifies that the resistance of the circuit is no longer thickness dependent and the film behaves as a semi-infinite layer[2,3]. However, this should be avoided when selecting the proper film thickness to operate at in that resistance changes will no longer be apparent. In addition to the pure film contribution, the solvent vapor adsorbing into the film will further increase the resistance.

Experimental

Poly(isobutylene) with a reported mass-average molecular weight of 420,000 was obtained from Sigma-Aldrich. Additionally, all of the solvents used in this work, HPLC grade and of 99.9+% purity, were purchased from this producer. To generate the required vapor, a specially designed dilution system, calibrated using a gas chromatograph, was utilized. Encased in a glass bubbler flask maintained at a constant temperature of 288.15 K in a refrigerated water bath, the solvent is charged with a certain flow rate of pure nitrogen forcing it to vaporize at a vapor pressure corresponding to the bubbler temperature. This pressure is approximated by the Wagner equation which is described later. The resulting vapor is further diluted by two pure nitrogen streams to the desired concentration, heated to the specified system temperature, 298.15 K, by means of a heating tape enveloping the stainless steel tubing, and delivered to the test cell. To achieve increasing solvent concentration levels, the flow of nitrogen entering the bubbler is increased while the dilution streams are decreased; however, the total nitrogen flow is kept at a constant 100 sccm. All three nitrogen streams were regulated by mass flow controllers. A more comprehensive description of the dilution system is available[4].

Manufactured by Maxtek, the TSM resonators operated at a base frequency of approximately 5 MHz. These TSM resonators were cleaned in a plasma cleaner to minimize debris adhered to the surface and spin-coated with the polymer film to the desired thickness. Spin-coating the polymer on the resonator ensures that the film is of finite thickness and uniform at the active area, the very center of the electrode. Once coated, the perturbed device was placed in a specially machined stainless steel test cell. The cell was designed with channels drilled in the top and bottom to allow refrigerated water to circulate through maintaining the cell and the TSM device with the polymer film at approximately 298.15 K, to within ± 0.1 K. Subsequent to coating and being enclosed in the test cell, the resonator is exposed to the generated vapor. The frequency response and the equivalent circuit parameters of the TSM device resulting from both the pure polymer film and the film with the adsorbed solvent vapor were measured by an Agilent 4294 A impedance analyzer. The entire experimental apparatus including the vapor generation and data acquisition was entirely automated and computer controlled through Labview 7.0.

Theory

The lumped parameter Butterworth-Van Dyke (BVD) model for the TSM device is well known[5]. In this model, changes in the electrical properties of the perturbed device associated with the addition of a polymer or polymer/solvent viscoelastic layer can be

represented as an additional motional impedance. Figure (1) depicts clearly the coated TSM device as represented by the BVD equivalent circuit.
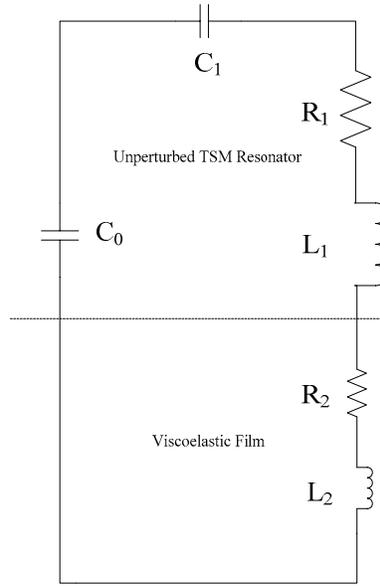

Figure 1: BVD equivalent circuit representing the polymer loaded TSM device

Hossenlopp *et al.,* (2004) have published the most recent description of this model in the context of relating the film contributed resistance, R_2, and inductance, L_2, to the coated viscoelastic film shear modulus, density and thickness, and the properties of the TSM resonator. These relations are as follows:

$$R_2 = \frac{N\pi}{4K^2\omega_s C_0}\left(\frac{\mathrm{Re}(Z_s)}{Z_q}\right) \quad (1)$$

$$L_2 = \frac{N\pi}{4K^2\omega_s^2 C_0}\left(\frac{\mathrm{Im}(Z_s)}{Z_q}\right) \quad (2)$$

$$Z_s = j(\rho_f G)^{1/2}\tan\left(\omega_s\left(\frac{\rho_f}{G}\right)^{1/2}h_f\right) \quad (3)$$

Here, N is the harmonic number (e.g. a harmonic number of one represents the natural frequency), K^2 is the electromechanical coupling coefficient having a value of 7.74×10^{-3} for AT-cut quartz crystal[6], ω_s is the angular frequency of the unperturbed TSM device defined by $2\pi f_r$, C_0 is the static capacitance that exists between the two electrodes, ρ_f and h_f are the density and thickness of the polymer film, respectively, and G is the complex shear modulus of the viscoelastic film.

Explicit expressions for the real and imaginary parts, $\text{Re}(Z_s)$ and $\text{Im}(Z_s)$, respectively, of the shear mechanical impedance Z_s are obtained by utilizing a Taylor series expansion of the tangent function in Equation (3). Retaining the first three terms of this series expansion and rearrangement yields explicit expressions for the storage and loss moduli of the viscoelastic film coating the TSM device[1]:

$$G' = \frac{B}{A^2 + B^2} \quad (4)$$

$$G'' = \frac{A}{A^2 + B^2} \quad (5)$$

such that

$$A = \left(\frac{\left(\frac{19\rho_f h_f}{24} - \frac{L_2}{A_0} \right) + \left[\left(\frac{L_2}{A_0} - \frac{19\rho_f h_f}{24} \right)^2 + \frac{R_2^2}{\omega_s^2 A_0^2} \right]^{\frac{1}{2}}}{\frac{4\omega_s^4 \rho_f^3 h_f^5}{15}} \right)^{\frac{1}{2}} \quad (6)$$

$$B = \frac{15 R_2}{4\omega_s^5 \rho_f^3 h_f^5 A_0 A} - \frac{5}{4\omega_s^2 \rho_f h_f^2} \quad (7)$$

with

$$A_0 = \frac{N\pi}{4 K_0^2 \omega_s C_0 \sqrt{\mu_q \rho_q}} \quad (8)$$

The quartz resonator properties are well known; however, accurate estimates for the film density and thickness are necessary to utilize the measured film TSM resonator equivalent circuit parameters R_2 and L_2 in approximating the shear moduli accurately.

Fortunately, the film thickness and density at each solvent concentration, C_1, given a reliable initial thickness, h_{f_o}, and reference density, ρ_{f_o}, of the polymer, can be approximated through the following expressions. The solution thermodynamic variables in Equations (9) through (11) are defined and evaluated below in the discussion of the polymer/solvent phase equilibrium.

$$h_f = h_{f_o} \left(\frac{1}{1 - w_1} \right) \quad (9)$$

$$\rho_f = \frac{\rho_{f_o} + C_1 M_1}{1 + C_1 V_1^{sat}} \qquad (10)$$

$$C_1 = \frac{\Phi_1}{V_1^{sat}(1 - \Phi_1)} \qquad (11)$$

For each exposed solvent concentration in the vapor phase, the solvent weight fraction in the polymer film was estimated using accurate polymer/solvent phase equilibrium data represented by a modified Flory-Huggins model given in Equations (12) through (14) below.

$$\ln(a_1) = \ln(1 - \Phi_2) + \left(1 - \frac{1}{r}\right)\Phi_2 + [2(A - B)\Phi_1 + B]\Phi_2^2 \qquad (12)$$

$$\Phi_i = \frac{V_i/M_i \, w_i}{\sum_i V_i/M_i \, w_i} \qquad (13)$$

$$a_1 = \frac{P_1 \exp\left[\frac{P}{RT}\left(B_{11} + \left(1 - \frac{P_1}{P}\right)^2 (2B_{13} - B_{11} - B_{33})\right)\right]}{P_1^{sat} \exp\left[\frac{B_{11}P_1^{sat}}{RT} + \frac{V_1^{sat}}{RT}(P - P_1^{sat})\right]} \qquad (14)$$

Where a_1 is the activity of the solvent in the polymer film, Φ_i and w_i are the volume and weight fractions, respectively, of a particular species, $i = 1$ representing the solvent and $i = 2$ the polymer, and r is the ratio of the specific volumes, V_2/V_1. These specific volumes were correlated as van der Waal volumes estimated through the summation of group volumes presented by Bondi[7,8]. The group volume of poly(isobutylene) was determined from the mass-average molecular weight to be 20,184 $cm^3 \cdot mol^{-1}$.

These equations are obtained upon equating the fugacities of the solvent in the vapor and polymer phases, and utilizing experimental polymer sorption data to estimate the A and B regression parameters in the modified Flory-Huggins model. Thus, these equations can be utilized to calculate the solvent weight fraction in the polymer film reliably. The various properties of the polymer and solvent utilized in this model are described below and listed in Tables (1) and (2).

The second virial coefficients of the pure solvent and solvent/nitrogen mixture, B_{11} and B_{13}, in that order, were calculated at 298.15 K from the Tsonopoulos correlation and are given in Table (1)[9]. B_{33}, the second virial coefficient of pure nitrogen, was additionally calculated from the Tsonopoulos correlation to be -5.4 $cm^3 \cdot mol^{-1}$.

Saturation pressure of the solvent in torr, P_1^{sat}, at the absolute system temperature, T, was estimated using an accurate correlation, Wagner's equation:

$$P_1^{sat} = \exp\left[(1-x)^{-1}\left(V_{PA}x + V_{PB}x^{1.5} + V_{PC}x^3 + V_{PC}x^6\right) + \ln(P_C)\right]$$

where $x = 1 - \dfrac{T}{T_C}$.

Here, P_C and T_C are the critical pressure and temperature of the solvent, respectively. The Wagner equation constants were taken from available literature and are presented in Table (1)[10].

To evaluate the saturation volume of the solvent, V_1^{sat}, the modified Rackett equation was employed:

$$V_1^{sat} = \frac{RT_C}{P_C} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]}$$

where $T_r = \dfrac{T}{T_C}$.

Z_{RA} is the Rackett compressibility factor[10].

A simple rearrangement of the ideal gas law applied to the solvent/nitrogen mixture and the substitution of the pure solvent concentrations generated by the calibrated dilution system into the resulting expression allows for the determination of the solvent partial pressure, P_1.

Results:

Preliminary results for the storage and loss moduli of poly(isobutylene) as a function of temperature plotted with available literature data are shown in Figure (2). With these results, we are able to deduce that the experimental apparatus and the shear modulus modeling are reliable. From this point, we can recommence the experiment to include the solvent exposure.
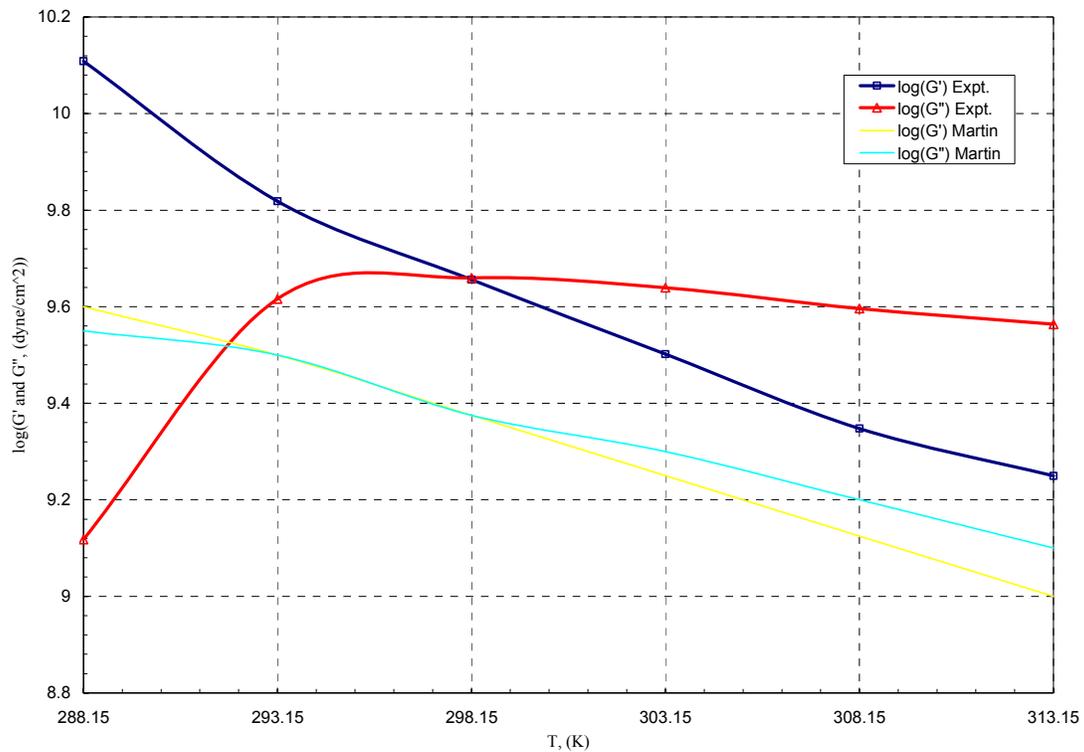

Figure 2: Storage and loss moduli of poly(isobutylene) as a function of absolute temperature

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Table 1:

Solvent	B_{11} $(cm^3 \cdot mol^{-1})$	B_{13} $(cm^3 \cdot mol^{-1})$	V_{PA}	V_{PB}	V_{PC}	V_{PD}
Benzene	-1677	-152	-6.98270	1.33210	-2.6286	-3.3340
Toluene	-2769	-183	-7.28607	1.38091	-2.8343	-2.7917
Hexane	-1965	-168	-7.46765	1.44211	-3.2822	-2.5094
Cyclohexane	-1862	-162	-6.96009	1.31328	-2.7568	-2.4549
Dichloromethane	-881	-114	-7.35739	2.75460	-4.0704	3.5070
Chloroform	-1259	-134	-6.95546	1.16625	-2.1397	-3.4442

Table 2:

Solvent	A	B	V_i $(cm^3 \cdot mol^{-1})$	Z_{RA}
Benzene	0.6169	1.1618	3.1878	0.2698
Toluene	0.6276	1.0126	3.9228	0.2644
Hexane	0.3471	0.8636	4.4998	0.2635
Cyclohexane	0.4544	0.6445	4.0464	0.2729
Dichloromethane	0.2540	1.5783	3.2479	0.2618
Chloroform	0.3174	1.0627	2.8700	0.2750