The application of reed-vibration mechanical spectroscopy for liquids to detect chemical reactions of an acrylic structural adhesive*

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There remain a number of unsolved problems about chemical reactions, and it is significant to explore new detection methods because they always offer some unique information about reactions from new points of view. For the first time, the solidification course of a modified two-component acrylic structural adhesive is measured by using reed-vibration mechanical spectroscopy for liquids (RMS-L) in this work, and results show that there are four sequential processes of mechanical spectra with time. The in-depth analyses indicate that RMS-L can detect in real-time the generation and disappearance of active free radicals, as well as the chemical cross-link processes in the adhesive. This kind of real-time detection will undoubtedly facilitate the study of the chemical reaction dynamics controlled by free radicals.

Keywords: mechanical spectroscopy, chemical reaction, acrylic structural adhesive

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1. Introduction

From macro to micro scales, knowledge of chemical reactions is continuously getting more and more distinct, and various detection methods have been introduced. However, there remain a number of unsolved problems about the reactions at present.[1,2] Obviously, it is significant to explore new detection methods because they always offer some unique information about chemical reactions from new points of view.

Recently, a new method called reed-vibration mechanical spectroscopy for liquids (RMS-L) was invented.[3–11] This method overcomes the shortcoming that traditional low-frequency mechanical spectroscopy cannot measure liquids,[3–18] and it is sensitive to measure Young's modulus and energy dissipation of liquids.[3–11] In this article, the RMS-L was used for the first time to detect the chemical reactions of a modified two-component acrylic structural adhesive, a typical liquid state system of chemical reactions, and the goal is to explore the detection feasibility of this method.

2. Experiment

The schematic diagram of RMS-L is shown in Fig. 1, and the measurement principle and steps are given below.[3–11]

1) Choose a proper substrate that is also used as the vibration reed for the RMS-L, and its surface should be treated specially, so that it can be infiltrated by the liquids to be measured.

2) Measure the internal friction (Q_s^{-1}) and resonance frequency (f_s) of the substrate reed versus temperature (T) and time (t). Then, Young's modulus (Y_s) of the reed versus T and t can be calculated by using the following formula:

$$Y_s = 0.0788\frac{\rho_s h_s w l_s^4}{I_1} f_s^2, \tag{1}$$

where ρ_s is the density of the substrate, $I_1 \equiv h_s^3 w/12$, w, h_s, and l_s are the width, thickness and length of the substrate reed, respectively, and 0.0788 is a constant related to the standing vibration with two nodes of the reed.[3]

3) Deposit a liquid sample on the surface of substrate and measure the internal friction (Q_c^{-1}) and resonance frequency (f_c) versus T and t of the combined system. Then, the complex Young's modulus ($Y = Y' + iY''$) of the deposited sample versus T and t can be calculated from the following formulae:

$$Y' = Y_s\frac{I_1}{I_{2d}}\left[\left(\frac{k}{\sqrt{f_s/f_c}-1+k}\right)^4\left(1+\frac{\rho_d h_d}{\rho_s h_s}\right)-\frac{I_{2s}}{I_1}\right], \tag{2}$$

$$Y'' = \frac{(2+k)Y'I_{2d}+2Y_sI_{2s}}{2kY_sI_{2s}}\frac{Y'I_{2d}+Y_sI_{2s}}{I_{2d}} \times (Q_c^{-1}-Q_s^{-1})+Y'Q_s^{-1}, \tag{3}$$

where Y' and Y'' are the real and imaginary part of the complex Young's modulus, respectively. Y' is usually called Young's modulus, and Y'' is related to the energy dissipation of the sample;[8–18] ρ_d and h_d are the density and thickness of the sample; $k \equiv l_d/l_s$, with l_d being the length of sample; $I_{2s} \equiv [(h_s - y_0)^3 + y_0^3]w/3$; $I_{2d} \equiv [(h_s + h_d - y_0)^3 - (h_s - y_0)^3]w/3$; $y_0 \equiv [1 + h_d Y'/(h_s Y_s)]h_s/2$ that can be calculated self-consistently according to Eq. (2).

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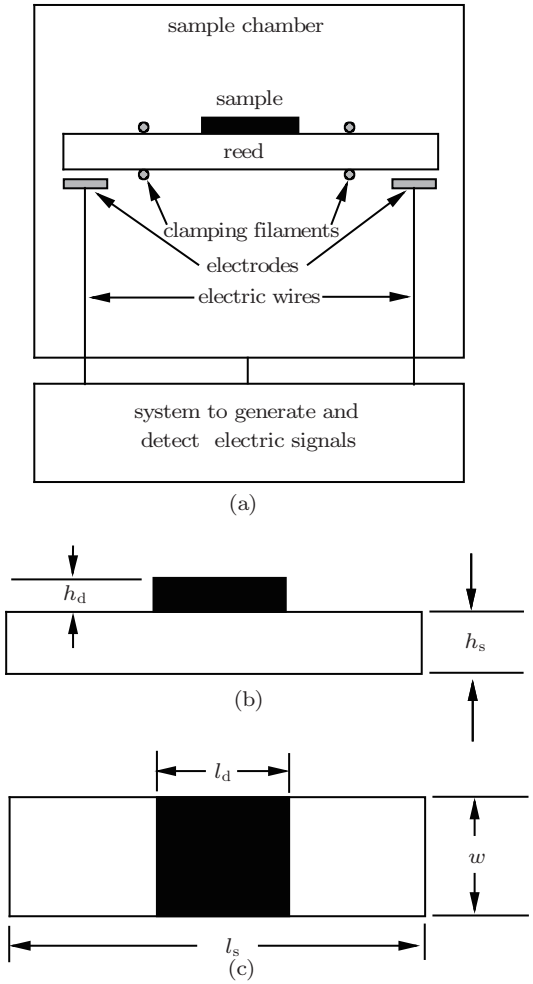


Fig. 1. (a) A schematic plot of detecting chemical reactions by RMS-L, where the reed is fixed at the two nodes of standing vibrations by NiCr clamping filaments with diameter of 0.1 mm, and the electrodes are used to excite and detect the reed vibrations; (b) a side elevation; (c) a planform of the reed and deposited sample.

Recently, Ying *et al.*[19] gave a general formula to calculate Y' and Y'' from f_c and Q_c^{-1} when the sample had an arbitrary area and was located at an arbitrary position on the substrate. This is undoubtedly useful to improve the RMS-L method. The results also show that equations (2) and (3) still hold when the sample is at the centre of the substrate for two node vibration measurements. The measurement setup in the present paper is just for this case, so we do the calculations still by using Eqs. (1)–(3).

The RMS-L device used in this article is homemade, and T is measured by a Cu-constantan thermocouple. The substrate used as the reed is made of monocrystalline silicon, whose size is $l_s \times w \times h_s = 40 \times 4 \times 0.4$ mm^3.

For the silicon substrate, $f_s = 2032$ Hz and $Q_s^{-1} = 8.25 \times 10^{-4}$ at 283 K, 1 atm, and 60% RH, and they scarcely change with t. At the moment that the sample is deposited onto the substrate, f_c $(t = 0)$ of the combined system is about 1997 Hz.

Modified two-component acrylic structural adhesive (AB adhesive) is fabricated by Fushun Geliahao Chemistry Co. Ltd., and its typical formula is shown in Table 1.

The mixture samples of components A and B detected in this paper are prepared in the following way. Take components A and B each of about 100 mg, and put them together on a glass slice, and stir them for about 10 s. Then, take the mixture of about 20 mg and put it on the substrate according to the manner as shown in Fig. 1, which takes about 1 min.

Direct observations using a microscope show that there are no cracks in the sample and no gaps between the sample and substrate during the whole measurement.

The sample chamber (Fig. 1(a)) is held in a thermostat, so that the sample could be kept in an environment with constant temperature, pressure, and humidity, which are 283 K with a fluctuation of about ± 1 K, 1 atm, and 60% RH in this paper, respectively.

Table 1. Ingredients of modified two-component acrylic structural adhesive.

Component	Name	Mass fraction/%	Effect
A	Methyl methacrylate	50–70	Monomer
	Methacrylic acid	5–20	Monomer, speed up solidification
	Hydroquinone	0.01–0.1	Stabilizer
	Antioxidant	0.01–10	Antioxidant
	Ethylene glycol	0.5–5	Solvent, antifreeze
	ABS resin	15–30	Plastic, reinforcer
	Isopropyl benzene hydroperoxide	1–5	Initiator
B	Methyl methacrylate	50–70	Monomer
	Methacrylic acid	5–20	Monomer, speed up solidification
	Hydroquinone	0.01–0.1	Stabilizer
	Butadiene acrylonitrile rubber	15–30	Toughener
	Amine accelerator	0.5–3	Accelerator
	Substituent thiourea	0.5–5	Accelerator
	Vanadium accelerator	0.01–2	Accelerator

3. Results and discussion

Figure 2 shows the variations of the measured resonance frequency (f_c), internal friction (Q_c^{-1}) and temperature (T) of the combined system of the combination AB and silicon substrate by RMS-L with time (t) at 283 K, 1 atm, and 60% RH.

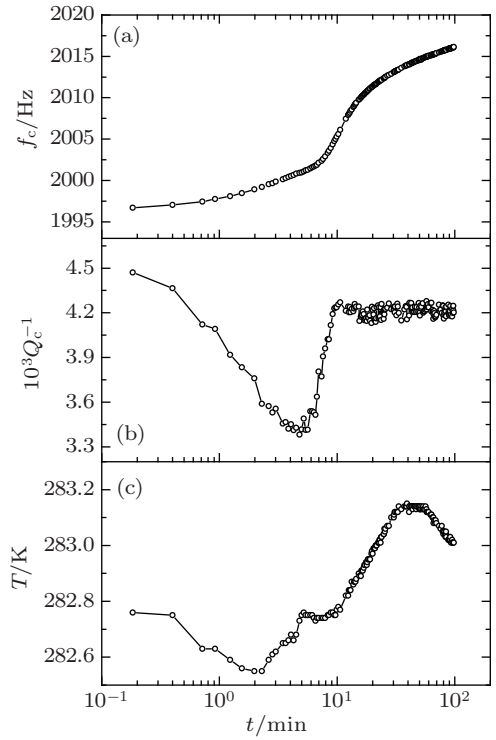


Fig. 2. Resonance frequency (f_c), internal friction (Q_c^{-1}), and temperature (T) of the combined system of the combination AB and the silicon substrate measured by RMS-L versus time at 283 K, 1 atm, and 60% RH.

The specific steps to calculate Y' and Y'' from f_c and Q_c^{-1} are as follows. 1) With the data of f_s, ρ_s, l_s, h_s, and w, Y_s is calculated from Eq. (1); 2) h_d is smaller and changes more or less with position. Here, the method to determine h_d is by assuming that $Y' = 0$ when $t = 0$, the effective value of h_d is calculated from Eq. (2) with the data of f_c ($t = 0$), f_s, ρ_s, ρ_d, h_s, k, and w, and h_d is assumed to be a constant throughout the measurement process; 3) with the data of f_c, Q_c^{-1}, f_s, Q_s^{-1}, Y_s, ρ_s, ρ_d, h_s, h_d, k (~ 0.1) and w, Y' and Y'' are calculated at each moment from Eqs. (2) and (3). The tiny measurement errors of k value have almost no effect on the normalized results of Y' and Y'' described below.[3]

From Fig. 2(c), it follows that the temperature of the combined system changes only 0.6 K in the whole measurement process, so it is speculated that the variations of f_c and Q_c^{-1} with t mainly stem from those of chemistry and structures.

The variations of calculated real (Y'/Y'_m) and imaginary part (Y'/Y'_m) of reduced complex Young's modulus, as well as internal friction ($Q^{-1} \equiv Y''/Y'$) of the combination AB at 283 K, 1 atm, and 60% RH with time are shown in Fig. 3. Here, Y'_m denotes the maximum of Y'. According to the more pronounced variations of Y'' with t, the solidification of combination AB can be divided into four sequential processes.

1) I^{AB} process for $t < t_1^{AB}$ (=2.1 min), where Y' increases rapidly and its increasing rate becomes small with t, while Y'' decreases slowly.

2) II^{AB} process for $t_1^{AB} < t < t_2^{AB}$ (=4.4 min), where Y' increases continuously with t, but Y'' decreases rapidly.

3) III^{AB} process for $t_2^{AB} < t < t_3^{AB}$ (=9.9 min), where Y' keeps increasing with t, but Y'' increases rapidly.

4) IV^{AB} process for $t > t_3^{AB}$, where Y' first increases and then tends to be a steady value with t, meanwhile Y'' increases only a little.

5) During the transition from III^{AB} to IV^{AB} process around t_3^{AB}, there is a step-like increase of Y'.

6) When $t \to 0$, Q^{-1} of combination AB is as high as about 4, which manifests the characteristic of viscoelastics.[8] At about 100 min, the Q^{-1} value is about 0.1, and it shows the characteristic of anelastics.[8]

The chemical reaction mechanism of AB adhesive is well known, and specifically, the initiators (oxidant) first react with the accelerators (reductant) to form active free radicals, which induce ethylenic linkages of methyl methacrylate to fracture and create new free radicals. The new radicals not only chain-react with methyl methacrylate, but also copolymerize with ABS resin and butadiene acrylonitrile rubber.

It is clear that the key ingredient of the above chemical reaction is the active free radicals, and it could be expected that the strong polarization field of the free radicals will enhance their correlations with the surrounding molecules. In other words, their random motions are limited by the field, so the energy dissipation turns lower, which results in the decrease of Y'' of the sample.[12–18] Moreover, the more the active free radicals, the lower the value of Y'' is. Based on this, we can find the correspondence between the above measured mechanical spectra and the solidification of AB adhesive as follows.

1) I^{AB} process of the mechanical spectra corresponds to that the initiators first react with accelerators to form a certain number of active free radicals, and they lead to the slow decrease of Y'' with t.

2) II^{AB} process corresponds to that the free radicals induce ethylenic linkages of methyl methacrylate to fracture and create a large number of new free radicals, and they lead to the rapid decrease of Y'' with t.

3) III^{AB} process corresponds to that the new free radicals not only chain-react with methyl methacrylate, but also copolymerize with ABS resin and butadiene acrylonitrile rubber, and their number decreases rapidly, which leads to the rapid increase of Y'' with t.

4) IV^{AB} process corresponds to that there are almost no free radicals, and Y'' is nearly kept unchanged with t.

5) The free radicals of I^{AB}, II^{AB}, and III^{AB} processes can not only chain-react with methyl methacrylate but also

copolymerize with ABS resin and butadiene acrylonitrile rubber, which inevitably leads to the increase in Y' with t.

6) The transition from $\mathrm{III}^{\mathrm{AB}}$ process to $\mathrm{IV}^{\mathrm{AB}}$ process around t_3^{AB} corresponds to the chain-reaction of methyl methacrylate, copolymerization of ABS resin, and butadiene acrylonitrile rubber, which necessarily leads to the step-like increase of Y'.

The above correspondence indicates that RMS-L can detect in real-time the generation and disappearance of active free radicals, as well as the chemical cross-link processes, and this kind of real-time detection will undoubtedly be of benefit to the study of chemical reaction dynamics of controlled free radicals.

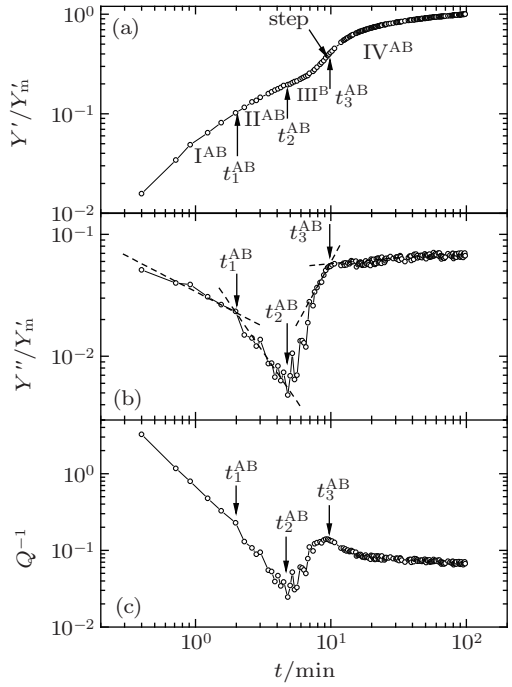


Fig. 3. Variations of (a) reduced real part (Y'/Y'_{m}) and (b) imaginary part (Y''/Y'_{m}) of complex Young's modulus, as well as (c) internal friction ($Q^{-1} = Y''/Y'$) of combination AB measured by RMS-L with t at 283 K, 1 atm, and 60% RH, where Y'_{m} is the maximum of Y'.

It should be noted that in the experimental results in Fig. 3, there exist some discrepancies with the low frequency mechanical spectra of the blends of polyester and triglycidyl-isocyanurate,[20] as well as epoxy resins and amine.[21] The main chemical reaction process of AB adhesive is the polymerization of small molecules, methyl methacrylate. Because one molecule usually contributes one free radical, the number of generated radicals is huge during the polymerization of methyl methacrylate. As ASB resin and butadiene acrylonitrile rubber in AB adhesive are all macromolecules, the number of the free radicals related to their polymerization is very small. Due to the chemical reactions in the blends of polyester/triglycidyl-isocyanurate[20] and epoxy-resins/amine[21] are also polymerization processes between macromolecules, the number of free radicals is very small, and gelation processes occur in these two mixtures. Therefore, the huge difference in radical number and the presence or absence of the gelation may be the microscopic origins of the different mechanical spectra.

4. Conclusions

In this paper, the solidification course of modified two-component acrylic structural adhesive is measured by using the RMS-L for the first time. The results show that there are four sequential processes of mechanical spectra during the solidification. The in-depth analyses indicate that RMS-L can detect in real time the generation and disappearance of active free radicals, as wells as the chemical cross-link process in the adhesive. This kind of real-time detection will undoubtedly be valuable to the study of the chemical reaction dynamics of controlled free radicals.

References

[1] Ananikov V P 2011 *Chem. Rev.* **111** 418
[2] Weldon M K and Friend C M 1996 *Chem. Rev.* **96** 1391
[3] Ying X N, Yuan Y H, Zhang L, Huang Y N, Wang Y N, Wang X L, Zhou D S and Xue G 2006 *Rev. Sci. Instrum.* **77** 053902
[4] Wu W H, Zhang J L, Zhou H W, Huang Y N, Zhang L and Ying X N 2008 *Appl. Phys. Lett.* **92** 011918
[5] Zhang J L, Zhou H W, Wu W H and Huang Y N 2008 *Appl. Phys. Lett.* **92** 131906
[6] Yuan Y H, Zhang L, Wang X L, Ying X N, Yan F, Huang Y N, Zhu J S and Wang Y N 2009 *Physica B* **404** 1862
[7] Yuan Y H, Ying X N and Huang Y N 2009 *Physica B* **404** 3771
[8] Huang Y N, Zhang J L and Ying X N 2006 *Prog. Phys.* **26** 359 (in Chinese)
[9] Zhou H W, Zhang J L, Huang Y N, Ying X N, Zhang L, Wu W H and Shen Y F 2007 *Acta Phys. Sin.* **56** 6547 (in Chinese)
[10] Guo X Z, Zhou H W, Zhang J L, Wu W H, Zhang J L and Huang Y N 2010 *Acta Phys. Sin.* **59** 417 (in Chinese)
[11] Zhou H W, Wang L N, Guo X Z, Wu N N, Zhang L, Zhang J L and Huang Y N 2010 *Acta Phys. Sin.* **59** 2120 (in Chinese)
[12] Nowick A S and Berry B S 1972 *Anelastic Relaxation in Crystalline Solid* (New York: Academic Press)
[13] Kě T S 1947 *Phys. Rev. B* **71** 533
[14] Kě T S 1947 *Phys. Rev. B* **72** 41
[15] Huang Y N, Wang Y N and Shen H M 1992 *Phys. Rev. B* **46** 3290
[16] Huang Y N, Wang Y N and Zhao Z X 1994 *Phys. Rev. B* **49** 1320
[17] Huang Y N, Wang C J and Riande E 2005 *J. Chem. Phys.* **122** 144502
[18] Huang Y N, Li X, Ding Y, Wang Y N, Shen H M, Zhang Z F, Fang C S, Zhuo S H and Fung P C W 1997 *Phys. Rev. B* **55** 16159
[19] Yuan Y H, Ying X N and and Zhang L 2011 *J. Appl. Phys.* **110** 053515
[20] Rmis X, Cadenato A, Morancho J M and Salla J M 2003 *Polymer* **44** 2067
[21] Kubisztal M, Haneczok G, Chrobak A, Kubik A and Rasek J 2009 *Mater. Sci. Eng. A* **521** 283