

# Analysis of gas sensing behaviors of carbon black/waterborne polyurethane composites in low concentration organic vapors

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Received: 13 February 2006 / Accepted: 6 June 2006 / Published online: 16 February 2007  
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**Abstract** Conductive composite comprised of carbon black and waterborn polyurethane was prepared by latex blending. It exhibited sensitivity to non-polar solvent vapors and polar solvent vapors as a result of the microphase separation structure of polyurethane. By studying the electrical response and absorption behaviors of the composite in low vapor pressure, a model based on Flory–Huggins principle was proposed to discuss the specific performance of the composite, including selective sensitivity, influences of vapor pressure and test temperature. Interaction between solvent and matrix polymer was proved to determine the maximum magnitude of response of the composite.

## Introduction

In recent years, electrically conductive polymer composites consisting of conductive fillers and insulating polymeric matrices have received increasing attention as their resistance varies with chemical solicitations

[1, 2]. When being exposed to organic vapors, the composites exhibit a drastic increase in their resistivity because solvents adsorption induced matrix swelling expands the inter-filler gap [3, 4]. Removal of the stimuli leads to desorption of the vapors and a decrease in electrical resistance back to the original values. On the basis of this feature, therefore, low cost solvent leak detectors and “electronic noses” can be prepared [5–7].

So far, many reports have been published in the very area, focusing on the response manners and their applications in either saturated [8–18] or low concentration organic vapors [19–27]. It is generally accepted that the maximum magnitudes of resistance variation of a given composite in response to different solvent vapors are different in the case of identical testing conditions. Besides its function as a measure for distinguishing solvent species, however, the selective sensitivity has not yet been studied in detail. The rule “like dissolves like” (i.e., a solvent that has a similar polarity to the composites’ matrix will usually be adsorbed by the substance very well), and similar solubility parameters of composites’ matrix and the solvent, were believed to be the prerequisites for an acceptable responsivity [1, 16, 17]. Nevertheless, the mechanism was challenged by the counterexample that the maximum electrical responses of carbon black/poly(butyl methacrylate) composites were independent on the differences in three dimensional solubility parameters of the matrix polymer and solvents when the sensing experiments were carried out under low vapor pressures [23].

The main interest of the present paper lies in analysis of the sensing ability and the related mechanism of conductive carbon black (CB) filled waterborne

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polyurethane (WPU) composites in different solvent vapors at low pressure, which is close to the actual working situation. Particular emphasis is laid on the interaction between vaporous analytes and the composites from the viewpoint of thermodynamics. The composite materials were selected because WPU is provided with good vapor transmission ability and CB/WPU proved to be a potential candidate for vapor sensor [15].

## Experimental

### Materials

Analytically pure ethylenediamine anhydrous (EDA), triethylamine (TEA) and dibutyltin dilaurate were dehydrated via 0.4 nm molecular sieves for more than 1 week prior to the experiments. Dimethylolpropionic acid (DMPA) was dried in vacuum at 80 °C for 24 h. Isophorone diisocyanate (IPDI) was used without further purification. Carbon black (type XC-72, specific surface area = 254 m<sup>2</sup>/g, DPB value = 174 ml/100 g, particle size = 50–70 nm), purchased from Cabot Co., was dried in vacuum at 110 °C for 48 h before use.

### Synthesis of WPU

The procedures for synthesizing WPU are described as follows. About 10 mmol of poly(tetramethylene ether glycol) (PTMEG, molecular weight = 2000), which acts as the soft segment of the WPU to be generated, was heated up to 120 °C in vacuum for 1 h, and then the system was filled up with nitrogen. About 10 mmol DMPA and 6 droplets of the catalyst (dibutyltin dilaurate) were added into the mixture after the system was cooled to 80 °C. Afterwards, 30 mmol IPDI in 10 ml butanone was drip-fed into the mixture. The reaction proceeded for 3 h. When the system was cooled to room temperature, the pre-polymer reacted with 10 mmol TEA for 1 h. Then, 100 ml distilled water and 10 mmol EDA were added to the pre-polymer with high-speed stirring. Twelve hours later, an emulsion of WPU was obtained.

### Preparation and characterization of the composites

For producing conductive composites, a certain amount of carbon black was added to the above WPU emulsion, and then the mixture was agitated by ultrasonic for 0.5 h and stirred for additional 4 h. Eventually, the pasty composites were coated onto an epoxy plate with comb electrodes [12]. Prior to further

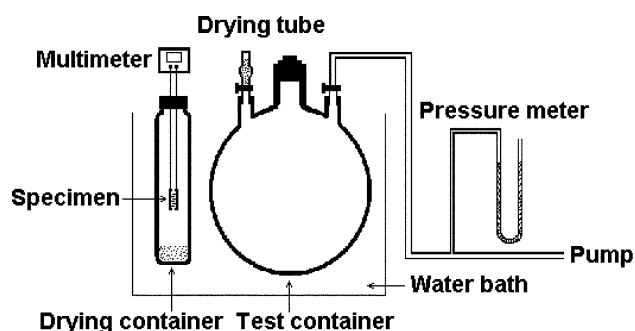
testing, the CB/WPU conductive composite films were dried at room temperature for 2 days and in vacuum for 2 days, respectively. The CB content of all the composites used in this work is fixed at 4.0 wt%, which is higher than the percolation threshold of the composites ( $\leq 1.5$  wt%).

Electrical resistance variation of the composites in response to various solvent vapors was measured as follows. A given volume of solvent was injected into the test container in advance. After 10 min, the comb electrodes with the composite film (40–60  $\mu\text{m}$  thick), hung in the drying container before test, were rapidly transferred to the test container. It is testified that the change in composites' resistance is negligible during the transfer. Then, time dependence of resistance of the specimen was recorded by a UT70C digital multimeter (Fig. 1). The vapor pressure was calculated by the thermodynamic equation of perfect gas, and the saturated vapor pressure was calculated in terms of Antoine equation. The corresponding responsivity is characterized by  $(R_t - R_0)/R_0$ , where  $R_t$  denotes the transient resistance and  $R_0$  the initial one in dry air. The maximal response is characterized by  $(R_{\text{max}} - R_0)/R_0$ , where  $R_{\text{max}}$  denotes the maximal resistance.

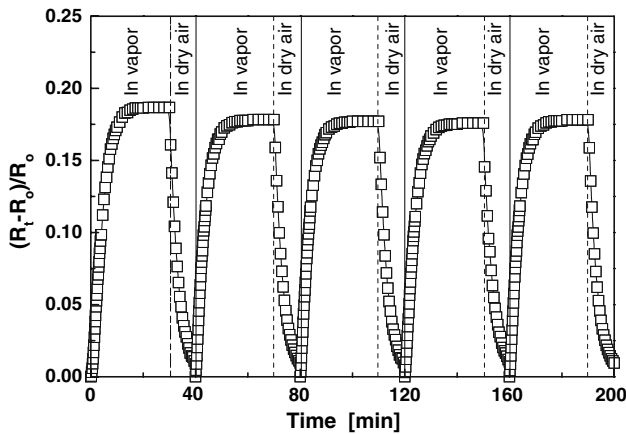
Solvent vapor adsorption behaviors and capacities of the composites were measured by an intelligent gravity analyzer (IGA-03, Hiden Co.). The precision of the system is about 0.1  $\mu\text{g}$ . The adsorbance is estimated by  $(M_t - M_0)/M_0$ , where  $M_t$  denote the absorbed mass of the specimen at transient state and  $M_0$  the initial mass of the specimen, respectively.

## Results and discussion

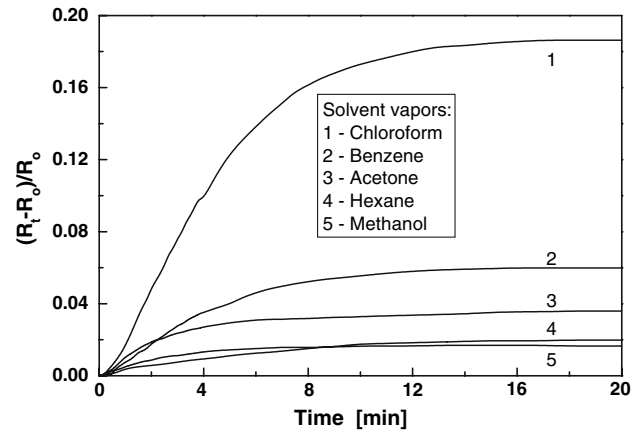
CB/WPU has been qualified as gas sensor in our previous work [15]. Its typical electrical response manner against chloroform vapor is shown in Fig. 2. Evidently,



**Fig. 1** Set-up for measuring electric resistance variation of the composite specimens in response to solvent vapor



**Fig. 2** Electrical responses of CB/WPU composite against chloroform vapor at a relative pressure of 0.01. The dash lines define the vapor absorption and desorption zones (testing temperature = 35 °C)

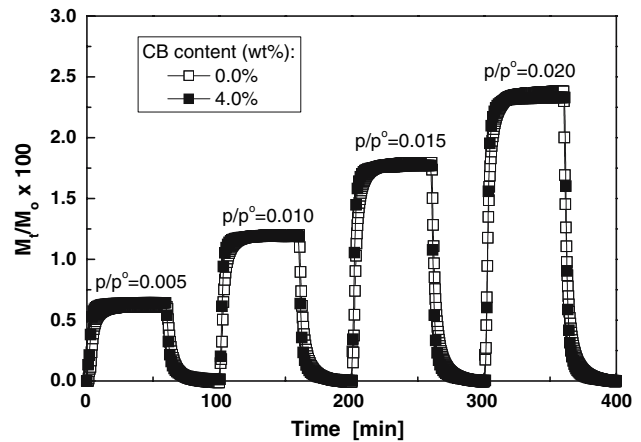


**Fig. 3** Time dependence of vapor induced resistance variation of CB/WPU composite in solvent vapors at a relative pressure of 0.01 (testing temperature = 35 °C)

the composite is able to offer reproducible responses to the organic gas in terms of resistance variation when the specimen repeatedly encounters the analyte and dry air. Besides, the composite exhibits different maximum responsivity (i.e., maximum variation in resistance) in the case of different vapors ranging from non-polar to polar (Fig. 3). Such a wide spectrum sensitivity was attributed to the microphase separation structure of the polyurethane macromolecules consisting of non-polar soft segments and polar hard segments [15]. The soft non-polar segments of the polyurethane (which constitute the majority of the polyurethane molecules) can be swollen by non-polar solvents, resulting in volume expansion induced resistance variation of the composite. For polar solvents, the hard polar segments of the polyurethane can be swollen accordingly, which leads to release of the soft segments from the restriction of the hard segments and hence the swelling of the entire composite.

However, the above explanation is not accurate enough. In the vapors of chloroform and acetone, for example, the composite’s maximum responsivity is quite different (Fig. 3) despite the fact that the solvents’ polarities, vapor pressures and solubility parameters are similar. In this context, analysis in terms of composites–solvent molecules interaction might help to reveal the hidden knowledge.

Figure 4 shows the results of solvent vapor adsorption experiments conducted on unfilled WPU and CB/WPU composite. Clearly, both adsorption and desorption behaviors of the materials are almost the same. Similar phenomenon was also found by Dong et al. [23]. It means that the adsorption of solvent vapors of the composite is mainly controlled by the



**Fig. 4** Time dependences of adsorbance of WPU and CB/WPU composite in chloroform vapor (testing temperature = 35 °C)

matrix polymer in the case of low CB loading (4 wt% in the present system). Therefore, the interaction between the adsorbed solvent molecules and the composite material can be represented by the interaction between the adsorbed solvent molecules and the chain segments of matrix polymer, regardless of the contribution of CB. On the basis of this simplification, Flory–Huggins theory is adopted [28, 29] to correlate the sorption isotherms:

$$\ln \alpha = \ln \phi_1 + \left(1 - \frac{1}{x}\right)\phi_2 + \chi_{12}\phi_2^2 \quad (1)$$

where  $\alpha$  denotes the activity of vapor,  $\phi_1$  and  $\phi_2$  the volume fractions of the adsorbed solvent vapor and the matrix polymer (supposing  $\phi_1 + \phi_2 = 1$ ), respectively,  $\chi_{12}$  the Flory–Huggins interaction parameter of the

adsorbed solvent vapor and the matrix polymer, and  $x$  the ratio of the molar volumes of the matrix polymer and the adsorbed solvent vapor.  $\chi_{12}$  is written as:

$$\chi_{12} = \frac{(Z - 2)\Delta\epsilon_{12}}{kT} \tag{2}$$

where  $Z$  is the lattice coordination number,  $k$  the Boltzmann constant, and  $\Delta\epsilon_{12}$  the change in energy for the formation of an unlike contact pair.

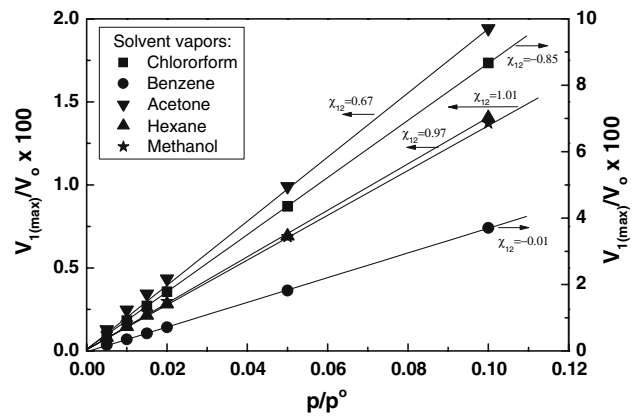
In the case of low vapor pressure, the adsorption capacity of the matrix polymer has to be so low that  $\phi_2$  can be regarded as 1, and the activity approximately equals to the relative vapor pressure,  $p/p^0$  (where  $p$  and  $p^0$  are the actual vapor pressure and saturated vapor pressure at testing temperature, respectively). Therefore, Eq. (1) is expressed as:

$$\ln \frac{p}{p^0} = \ln \phi_1 + (1 + \chi_{12}) \tag{3}$$

Because the value of  $\phi_1$  is also rather small for low concentration vapor, it can be calculated by the measurable  $V_{1(\max)}/V_0$ , where  $V_{1(\max)}$  and  $V_0$  denote the maximum volume of the vapor adsorbed by the composites under certain pressure and the initial volume of the composites, respectively. Accordingly, Eq. (3) is converted to:

$$\frac{V_{1(\max)}}{V_0} = e^{-(1+\chi_{12})} \frac{p}{p^0} \tag{4}$$

From Eq. (4), it is seen that the equilibrium adsorption capacity of the composites,  $V_{1(\max)}/V_0$ , is proportional to the relative vapor pressure at a certain temperature, and the slope of the linear regression equals to  $e^{-(1+\chi_{12})}$ . To verify this estimation,  $V_{1(\max)}/V_0$  is measured as a function of  $p/p^0$  (Fig. 5). Clearly, the relationship shown in Eq. (4) well fits the experimental data, which proves the above deduction. Besides, the Flory–Huggins interaction parameters of the solvent–WPU pairs can be calculated from the slopes, as marked besides the corresponding plots in Fig. 5. For chloroform and benzene vapors, the values of  $\chi_{12}$  are negative, meaning the solvent vapors are easy to be adsorbed by the WPU composite. When methanol vapor is used, the Flory–Huggins parameter is greater than 1, so that the vapor is difficult to be adsorbed by the composites. Comparatively, the Flory–Huggins parameters of the systems of acetone–WPU and hexane–WPU are greater than 0.5 but less than 1. The composite’s adsorbability of the two vapors should be higher than that of methanol.

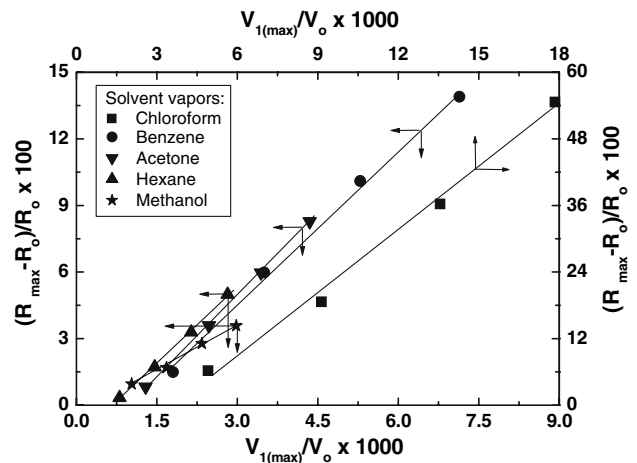


**Fig. 5** Equilibrium adsorption capacity of CB/WPU composite as a function of relative pressure in different solvent vapors (testing temperature = 35 °C)

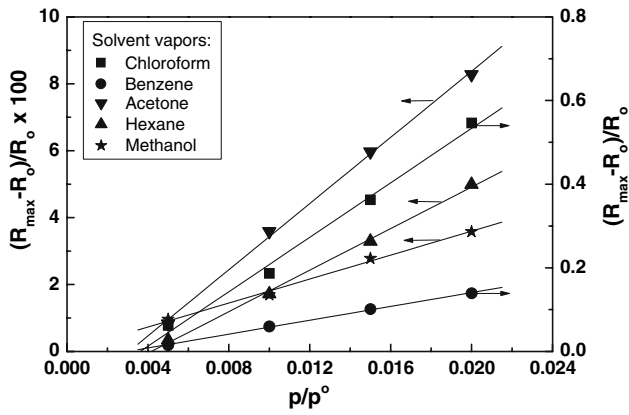
In consideration of the fact that the magnitude of a composite’s electrical response is a function of the quantity of the adsorbed solvent vapor [23], it is natural to correlate the maximum responsivity,  $(R_{\max} - R_0)/R_0$ , with the equilibrium adsorption capacity of the composites,  $V_{1(\max)}/V_0$ . As shown in Fig. 6, there are linear relationships between  $(R_{\max} - R_0)/R_0$  and  $V_{1(\max)}/V_0$  when the composites were tested in different vapors, which can be described by:

$$\frac{R_{\max} - R_0}{R_0} = k_1 \frac{V_{1(\max)}}{V_0} + k_2 \tag{5}$$

where  $k_1$  and  $k_2$  are constants depending on solvent species. As  $(R_{\max} - R_0)/R_0$  can’t be negative when the aforesaid swelling model works, Eq. (5) is valid only



**Fig. 6** Maximum magnitude of resistance variation of CB/WPU composite in response to solvent vapors as a function of the composite’s equilibrium adsorption capacity (testing temperature = 35 °C)

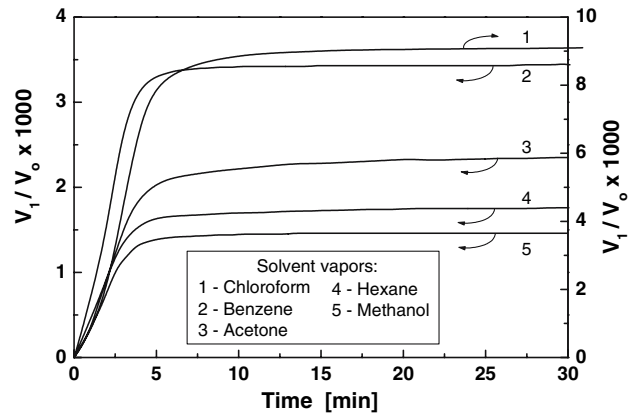


**Fig. 7** Maximum magnitude of resistance variation of CB/WPU composite in response to solvent vapors as a function of relative pressure of the vapors (testing temperature = 35 °C)

within a certain range of  $V_{1(max)}/V_0$ . Reasonable caution should be excised when extrapolating. Inserting Eq. (4) into Eq. (5), we have:

$$\frac{R_{max} - R_0}{R_0} = k_1 e^{-(1+\chi_{12}) \frac{p}{p^0}} + k_2 \quad (6)$$

Since  $\chi_{12}$  is temperature dependent, the electrical response of a conductive composite against a given solvent vapor under constant temperature should be proportional to  $p/p^0$  as deduced from Eq. (6). This is confirmed by the linear plots in Fig. 7. In fact, such linear dependence of the maximum responsivity on vapor pressure has been widely detected [24, 25, 30, 31]. According to Eq. (6), it is known that the slopes of these linear regressions,  $\sim e^{-(1+\chi_{12})}$ , are closely related to the Flory–Huggins interaction parameter. That is, the interaction between the solvent molecules and the composite’s matrix determines the magnitude of resistance variation in response to solvent vapor. This explains the reason why the composites possess selective gas sensitivity. As illustrated in Fig. 5, both the  $\chi_{12}$  values of the systems chloroform–WPU and benzene–WPU are negative, but the former one is much lower, so that the composite exhibits higher equilibrium adsorption capacity (Fig. 8) and maximum responsivity (Fig. 3) when being tested in chloroform vapor. Similarly, the vapor adsorption and sensitivity of the composite in other solvent vapors also rank in the inverse order of the  $\chi_{12}$  values. As predicted by Eq. (6), under given temperature and relative pressure, higher  $\chi_{12}$  results in lower equilibrium adsorption capacity and maximum responsivity, and vice versa.



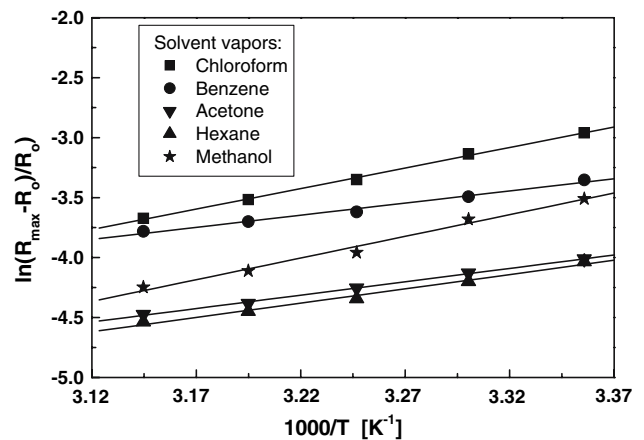
**Fig. 8** Time dependence of volume adsorption,  $V_1/V_0$  (where  $V_1$  and  $V_0$  denote the transient volume of the vapor adsorbed by the composite under certain pressure and the initial volume of the composite, respectively), of CB/WPU composite in different solvent vapors (testing temperature = 35°C,  $p/p^0 = 0.01$ )

In fact, Eq. (6) also describes the influence of temperature. By taking the natural logarithm of both sides of the equation and supposing  $k_2$  is negligible, the maximum responsivity appears to be:

$$\ln\left(\frac{R_{max} - R_0}{R_0}\right) = -\chi_{12} + \left(\ln \frac{p}{p^0} + \ln k_1 - 1\right) \quad (7)$$

It is known that saturated vapor pressure can be correlated with temperature through the Antoine–Equation [32]:

$$\log p^0 = A - \frac{B}{C + T - 273.15} \quad (8)$$



**Fig. 9** Logarithm of the maximum responsivity of CB/WPU composite in various solvent vapors versus inverse temperature at a constant vapor pressure of 100 Pa

where  $A$ ,  $B$  and  $C$  are constants in relation to solvent species and can be found in Ref. [34] for different solvents, and  $T$  is Kelvin temperature. Combining Eqs. (2), (7) and (8), the temperature dependence of maximum responsivity is yielded:

$$\ln\left(\frac{R_{\max} - R_0}{R_0}\right) \approx \frac{2.3B - (Z - 2)\Delta\varepsilon_{12}/k}{T + C - 273.15} + (\ln p + \ln k_1 - 1 - 2.3A) \quad (9)$$

According to Eq. (9),  $\ln(R_{\max} - R_0)/R_0$  should increase with  $1/T$  in the form of a linear function at fixed vapor pressure. This is evidenced not only by the WPU based composite (Fig. 9) but also by the results of other researchers [33, 34]. Because of the Arrhenius-like dependence, it can be phenomenologically deduced that thermal activation governs the response process when temperature changes [24].

## Conclusions

The CB/WPU composites, prepared by latex blending, exhibit sensitivity to either non-polar solvent vapors or polar solvent vapors. The Flory–Huggins interaction parameter determines the composites' maximum responsivity in vapors, and hence the selective sensitivity. At a constant temperature, the slopes of the linear dependence of the maximum magnitude of resistance variation in response to solvent vapors on relative pressure of the vapors are a function of the Flory–Huggins parameter. Besides, logarithmic maximum responsivity of the composites varies linearly with inverted temperature under fixed vapor pressure.

**Acknowledgements** The authors would like to thank the financial supports of the Natural Science Foundation of China (Grant 50133020), the Team Project of the Natural Science Foundation of Guangdong (Grant 20003038) and the Talent Training Program Foundation of the Higher Education Department of Guangdong Province.

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