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Examination of the surface properties of kaolinites by inverse gas chromatography: Dispersive properties

Young Cheol Yang† **and Pyoung Ran Yoon**

Dep't of Mineral Resources & Energy Eng., Chonbuk National Univ., Jeonju 561-756, Korea

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Abstract−The application of inverse gas chromatography (IGC) for the examination of the surface properties of untreated kaolinite and kaolinites surface-treated with titanate coupling agents is discussed. This paper presents and discusses the dispersive properties expressed by γ_S^D, the dispersive component of the surface free energy, as determined at various temperatures. The γ_S^D values of all the samples were negatively correlated with the temperature of IGC measurement. At the same temperature of IGC measurement, the values of γ_S^D determined by IGC were significantly lower for the surface-treated kaolinites than for the untreated ones. The γ_S^D value of the kaolinite surface-treated with isopropyl triisostearoyl titanate (ITT) at 150 °C exhibited a surface energy close to that (28.3 mJm^{-2}) of polyethylene with no surface polarity.

Key words: Inverse Gas Chromatography (IGC), Kaolinite, Dispersive Component of the Surface Free Energy (γ_S^D)

GENERAL

1. Introduction

Kaolinite, a clay mineral, has a broad variety of applications in industry [Jepson, 1984]. Kaolinite has been treated with surface-modifying agents to obtain improved dispersibility, electrical properties, water resistance and reinforcement in plastics systems [Katz, 1978]. In this study, we used titanate coupling agents as surface-modifying agents for kaolinite.

The mechanical performance of a composite material strongly depends on the properties of the filler-matrix interface and, in particular, on the level of adhesion between the matrix and the reinforcing filler. The level of adhesion is determined by the surface energies of both adherents. The surface free energy which describes the interaction potential of a given surface has two components: the dispersive component originating from dispersive or London interactions, and the specific component due to all other types of interactions.

Inverse gas chromatography (IGC) at infinite dilution conditions may be successfully applied to the determination of surface properties of various solids [Dorris and Gray, 1980]. IGC allows the detection of the solid surface properties, using molecules of known properties, or probes, which are injected in a chromatographic column filled with the solid of interest.

Finally, we chose IGC for the detection of eventual differences in the γ_S^D values of untreated kaolinite and kaolinites surface-treated with titanate coupling agents. The IGC results are reported in this paper.

2. Theory of Inverse Gas Chromatography (IGC) at Infinite Dilution

In IGC at infinite dilution condition, the retention volume V_N is computed from the following expression (1):

$$V_N=(t_R-t_0)jD_C \tag{1}$$

where t_R is the retention time of the probes; t_0, the zero retention time measured with a nonadsorbing probe such as methane; j, the compressibility factor depending on the pressure at column inlet and outlet, and D_C, the corrected flow rate. Practically, the retention time and the retention volume V_N can be determined as in a current chromatographic experiment: a larger V_N will correspond to a higher affinity of the probe for the chromatographic support.

In expression (1), j was calculated by the following expression (2) [James and Martin, 1952]:

$$j=1.5\left[\frac{(p_i/p_0)^2-1}{(p_i/p_0)^3-1}\right] \tag{2}$$

where p_i is the inlet pressure of the carrier gas (atm), and p_0 the outlet pressure of the carrier gas (atm) which usually equals atmospheric pressure.

For a test substance, the free energy of adsorption, ΔG_A is the sum of the energies of adsorption attributable to dispersive and specific interactions. Adsorption of non-polar probes such as n-alkanes occurs through dispersive interaction, whereas for polar probes both London and acid-base interactions contribute to ΔG_A. In this study, we used the model of Donnet et al. because the injected probe is a gas state [Donnet et al., 1991]. In this model, ΔG_A is given by the following expressions:

$$[-\Delta G_A]=[-\Delta G_A^D]+[-\Delta G_A^{SP}] \tag{3}$$

$$=[RT\ln V_N+C] \tag{4}$$

$$=[K\cdot(h\nu_S)^{1/2}\cdot\alpha_{0S}\cdot(h\nu_L)^{1/2}\cdot\alpha_{0L}]+[-\Delta G_A^{SP}] \tag{5}$$

where ΔG_A^D and ΔG_A^{SP} are the dispersive and specific components of the free energy of adsorption, respectively. The value of the constant, C, in expression (4) depends on the arbitrarily chosen reference state of the adsorbed molecule. In expression (5), K is a constant, h planck's constant, and α_0 the deformation polarizability of the molecules. Subscripts S and L refer to solid and liquid, respectively. In the case of n-alkanes, ΔG_A is equal to the free energy of

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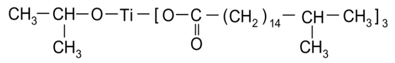
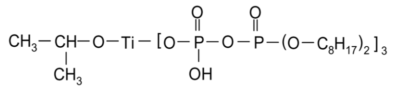
†To whom correspondence should be addressed.

E-mail: yang072@chonbuk.ac.kr

Table 1. Chemical names and structures of the titanate coupling agents

Chemical name	Structure
Isopropyltriiso-stearoyltitanate	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-O-Ti-[O-\underset{O}{\underset{\Vert}{C}}-(CH_2)_{14}-\underset{CH_3}{\underset{\mid}{CH}}-CH_3]_3$
Isopropyltri(dioctylpyro-phosphato)titanate	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-O-Ti-[O-\overset{O}{\overset{\Vert}{\underset{OH}{\underset{\mid}{P}}}}-O-\overset{O}{\overset{\Vert}{P}}-(O-C_8H_{17})_2]_3$

adsorption corresponding to dispersive interactions ΔG_A^D only, i.e., $[-\Delta G_A^{SP}]=0$ in expression (5). The term $[K\cdot(h\nu_S)^{1/2}\cdot\alpha_{0S}]$ is characteristic of a given solid surface and is related to ΔG_A^D. Consequently, $[RT\ln V_N+C]$, between adsorbate-adsorbent, appears as a linear equation of the parameter $[(h\nu_L)^{1/2}\cdot\alpha_{0L}]$, and $[K\cdot(h\nu_S)^{1/2}\cdot\alpha_{0S}]$ becomes the slope of the linear equation.

The above method has been used to characterize silicas, modified silicas, oxides, various minerals and solid polymers [Balad et al., 1988; Papier et al., 1987; Sidqi et al., 1989; Chehimi and Pigois-Landureau, 1994; Panzer and Schreiber, 1992; Voekel et al., 1993].

EXPERIMENTAL

1. Materials

The natural kaolinite used in this work was sourced from Indonesia. The titanate coupling agents used in the adsorption experiment were isopropyl triisostearoyl titanate (ITT) and isopropyl tri(dioctylpyrophosphato) titanate (ITDT). The chemical names and structures of these coupling agents are shown in Table 1 [Monte and Sugerman, 1978]. In order to modify the kaolinite surface, ITT and ITDT were dissolved in hexane (C_6H_{14}) and methyl ethyl ketone (2-butanone, $C_2H_5COCH_3$), respectively.

2. Adsorption Experiment

The experiment to modify the kaolinite surface was performed as follows. Solvent (100 ml), titanate coupling agents (0.4 to 3.0 g) and kaolinite (20 g) were stirred by magnetic bar stirrer for an hour and then separated into solid and liquid components by a centrifugal separator. The separated kaolinites were then dried for 6 hours at 105 °C. Three types of samples were prepared in this way for IGC study at infinite dilution: untreated kaolinite, ITT-treated kaolinites and ITDT-treated kaolinites.

3. IGC Experiment Conditions

Since the particle size of kaolinite was too small for making chromatographic supports, kaolinite disks were prepared by compression of the powders in an IR die, under a pressure of 10^8 Pa. The disks were then hand-crushed and sieved to select the fraction of particles having diameters between 250 and 425 μm. Particles of the correct size were introduced into a stainless steel column, 50 cm long and 3.17 mm in diameter. Approximately 1 g of each sample was used as the chromatographic column filling. Each column, filled with sample, was conditioned at 200 °C for 24 hours to remove any impurities in the column. IGC measurements were made with a Hewlett Packard 6890 GC System, equipped with a highly sensitive flame ionization detector (FID). The carrier gas was nitrogen (N_2) and the flow rate was 20 ml/min. The temperature of IGC measurement was varied from 110 to 200 °C. Very small amounts of probes were injected by using the following stratagem: 1 to 5 μl of probe was introduced via a septum in a 1 L flask, which was flushed with N_2, after which 0.05 ml of the diluted probe was injected in the GC System. A homologous series of n-alkanes, C_5 to C_{10}, were used as the probe in the IGC experiment.

RESULTS AND DISCUSSION

The dispersive component of the surface free energy, γ_S^D, is obtained by injecting a homologous series of n-alkanes into the column and determining their retention characteristics. Dorris and Gray have used the incremental amount of free energy of adsorption corresponding to the adsorption of one CH_2 group, $\Delta G_A^{CH_2}$, to determine γ_S^D [Dorris and Gray, 1980]:

$$\gamma_S^D=\frac{1}{4\gamma_{CH_2}}\left[\frac{\Delta G_A^{CH_2}}{N\cdot a_{CH_2}}\right]^2 \tag{6}$$

where γ_{CH_2} is the surface energy of a solid composed solely of -CH_2- groups, i.e., a surface analogous to polyethylene; N, Avogadro's number, and a_{CH_2}, the cross sectional area of an adsorbed -CH_2- group (0.06 nm^2) [Dorris and Gray, 1980]. The variation of γ_{CH_2} with temperature is given by:

$$\gamma_{CH_2}=35.6+0.058(293-T)\ \text{in mJm}^{-2} \tag{7}$$

where T is the temperature in K.

Generally, the logarithm of V_N varies linearly with the number of carbon atoms of the injected n-alkanes. Therefore, it becomes possible to define the free energy of adsorption, $\Delta G_A^{CH_2}$, of one methylene group, which no longer depends on the arbitrary choice of the reference state:

$$\Delta G_A^{CH_2}=-RT\ln\left(\frac{V_N^{n+1}}{V_N^n}\right) \tag{8}$$

where R is the ideal gas constant; T, the absolute temperature, and

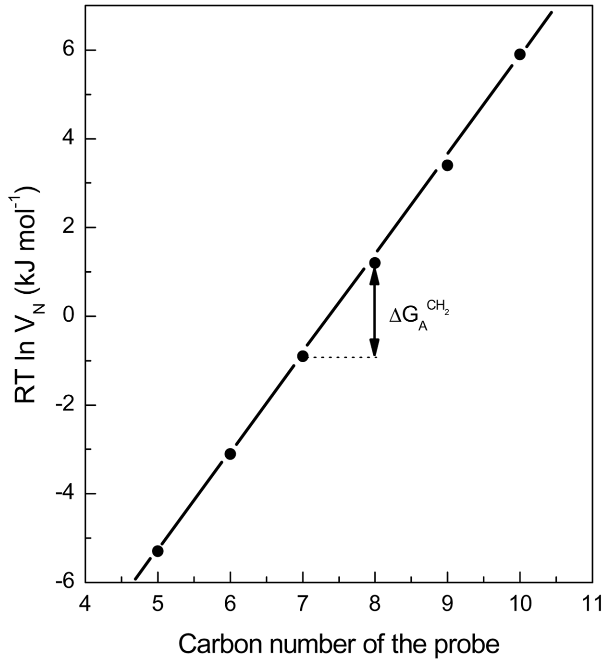


Fig. 1. Determination of the $\Delta G_A^{CH_2}$ value.

V_N^{n+1} and V_N^n, the net retention volumes of n-alkanes having n+1 and carbon atoms, respectively.

In the IGC experiment, the retention time and volume are associated with the γ_S^D of the solid. That is, $RT\ln V_N$ varies linearly with the number of carbon atoms of the injected n-alkanes, as shown in Fig. 1.

In Fig. 1, $\Delta G_A^{CH_2}$ is the slope of the line from expression (8). Therefore, the γ_S^D values of the solid are computed by expression (6).

Figs. 2 and 3 display the variation of [$RT\ln V_N$] vs. carbon number of the n-alkanes used to probe the surface properties of the kaolinites surface-treated with ITT and ITDT, respectively. Each line

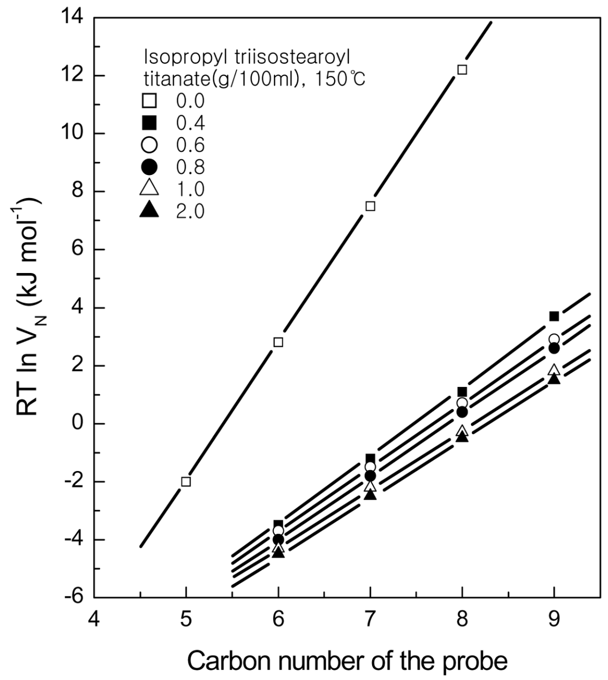


Fig. 2. Variation of [$RT\ln V_N$] vs. carbon number of the n-alkanes used as molecular probes for the untreated and surface-treated kaolinites with isopropyl triisostearoyl titanate.

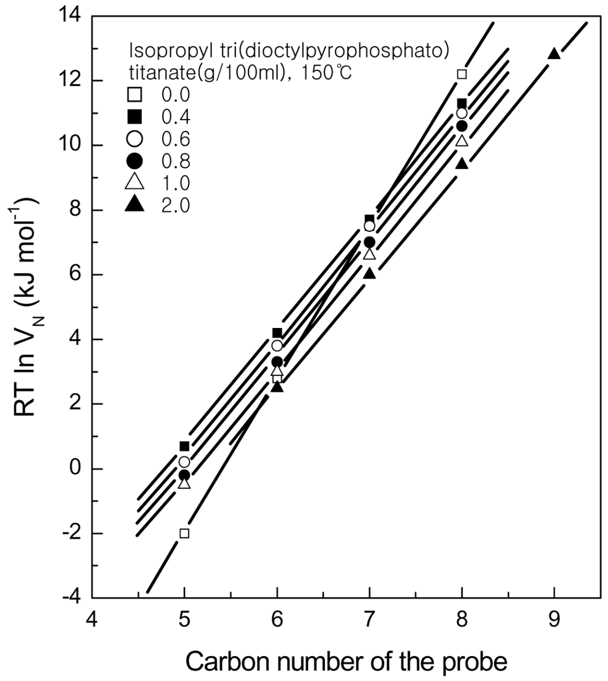


Fig. 3. Variation of [$RT\ln V_N$] vs. carbon number of the n-alkanes used as molecular probes for the untreated and surface-treated kaolinites with isopropyl tri(dioctylpyrophosphato) titanate.

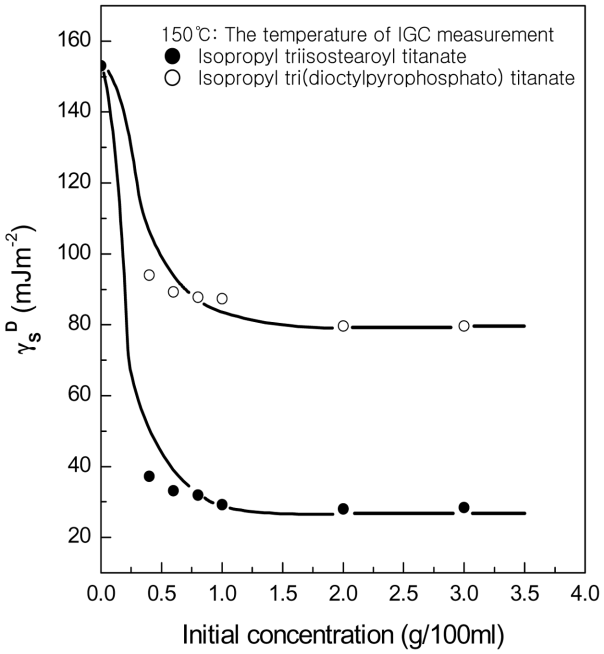


Fig. 4. Dispersive component of the surface free energy (γ_S^D) vs. initial concentration of titanate coupling agents.

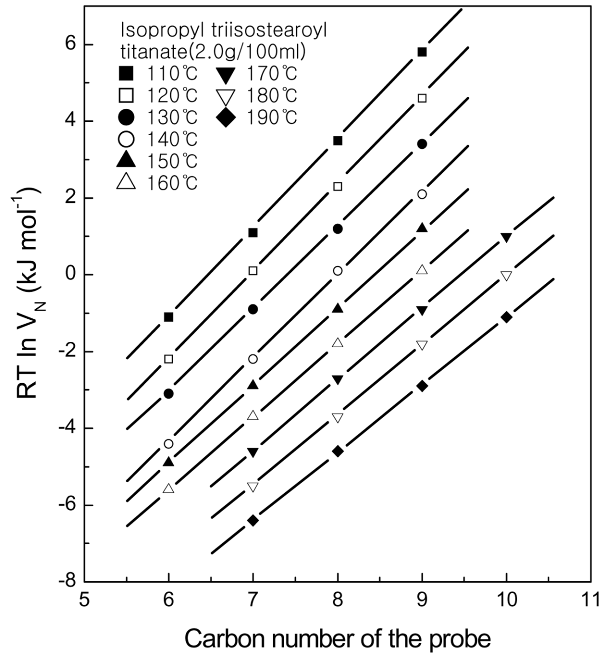


Fig. 5. Variation of [$RT\ln V_N$] vs. carbon number of the n-alkanes used as molecular probes for the surface-treated kaolinite with isopropyl triisostearoyl titanate.

indicates the variation according to the concentrations of ITT and ITDT. The γ_S^D values of the kaolinites surface-treated with ITT and ITDT were computed by the above method for each line.

Fig. 4 displays the variation of the γ_S^D values of the kaolinites surface-treated with ITT and ITDT. The values of γ_S^D decreased significantly when the concentration of the coupling agents was increased for the two types of titanate coupling agents. But there was no variation of γ_S^D with the variant concentration when this concentration exceeded approximately 1.5 g/100 ml. In the case of ITDT, the values of γ_S^D were larger than those of ITT at the same concentration.

The measurement of RTlnV$_N$ according to the measuring temperature was conducted for samples of 2.0 g/100 ml concentration of ITT and ITDT, because the results presented in Fig. 4 suggested that the maximum adsorption of titanate coupling agents was achieved at this concentration.

Figs. 5 and 6 display the variation of [RTlnV$_N$] vs. carbon number of the n-alkanes used to probe the surface properties of the kaolinites surface-treated with ITT and ITDT, respectively. Each line indicates the variation according to the temperature of IGC measurement.

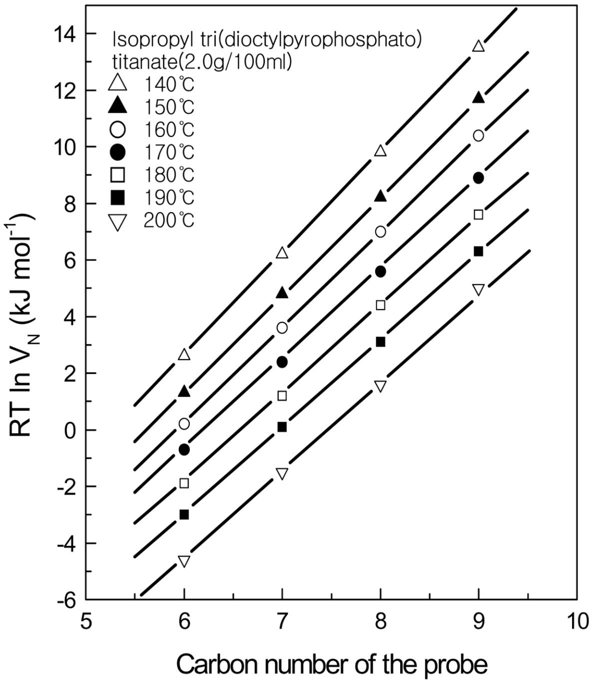


Fig. 6. Variation of [RTlnV$_N$] vs. carbon number of the n-alkanes used as molecular probes for the surface-treated kaolinite with isopropyl tri(dioctylpyrophosphato) titanate.

The γ_S^D values of the three types of kaolinite were computed at various measuring temperatures between 110 and 200 °C. The calculated values of γ_S^D are presented in Table 2. The values of γ_S^D decreased with increasing measuring temperature for all the samples except a few cases where γ_S^D increased slightly. In the γ_S^D values of the ITT-surface-treated kaolinite, the value of γ_S^D was about 28.4 mJm^{-2} at 150 °C, which is approximately the same as the reported value of 28.29 mJm^{-2} at 150 °C for a solid surface composed solely of alkyl chains such as a nonpolar polyethylene [Wu, 1974]. The γ_S^D values of the ITT-surface-treated kaolinite were slightly lower than those of a solid surface such as polyethylene at over 150 °C. Nevertheless, the dispersibility of the ITT-surface-treated kaolinite was thought to be acceptable in a polymer such as polyethylene when considered over the whole range of measuring temperature, as shown Table 2.

The γ_S^D values of the ITDT-surface-treated kaolinite were significantly higher than those of the ITT-surface-treated kaolinite at the same measuring temperature. Consequently, the dispersibility of the ITDT-surface-treated kaolinite was considered to be suitable for a polymer with high surface energy such as poly(ethylene terephthalate) (PET) with 30 mJm^{-2}, and a nylon polyamide compound with 29.0 mJm^{-2} at 290 °C [Wu, 1974].

CONCLUSIONS

A raw kaolinite underwent surface treatment with two types of titanate coupling agents: ITT and ITDT. The processing of the raw kaolinite by these titanate coupling agents modified the kaolinite surface. We examined the surface properties of these kaolinites according to γ_S^D using IGC. The present study produced the following conclusions:

1. The titanate coupling agents reduced significantly the γ_S^D value of the kaolinite surface compared to that of the untreated kaolinite.
2. The values of γ_S^D decreased with increasing IGC measuring temperature for almost all the cases.
3. The γ_S^D values of the ITDT-surface-treated kaolinite were significantly higher than those of the ITT-surface-treated kaolinite. This result indicates that while the ITT-surface-treated kaolinite is suitable for a polymer such as polyethylene, the ITDT-surface-treated kaolinite is suitable for a polymer with a high γ_S^D value such as

Table 2. Dispersive component of the surface free energy, γ_S^D of the untreated and surface treated kaolinites with titanate coupling agents (2.0 g/100 ml)

Sample	γ_S^D (mJm^{-2})									
	110 °C	120 °C	130 °C	140 °C	150 °C	160 °C	170 °C	180 °C	190 °C	200 °C
Untreated kaolinite					153.3	150.9	138.5	135.9	131.5	128.9
Surface treated kaolinite with isopropyltriisostearoyltitanate	34.6	32.3	31.9	30.7	28.4	25.5	25.8	24.3	23.6	
Surface treated kaolinite with isopropyltri(dioctylpyrophosphato) titanate				87.2	79.6	80.1	71.8	71.9	70.6	66.8
Linear polyethylene[a]	30.57	30.0	29.43	28.8	28.29	27.72	27.15	26.58	26.01	

[a] Calculated from Ref. [Wu, 1974].

poly(ethylene terephthalate) (PET) or a nylon polyamide compound.

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