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Gaseous thermal conductivities of new hydrofluoroethers (HFEs)

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Abstract

The gaseous thermal conductivities of 15 new hydrofluoroethers (HFEs) were measured by a steady state coaxial cylinder method. The results were compared with those obtained separately by a transient hot-wire method. Deviations between the two methods are less than 3.4%. In comparison with hydrofluorocarbons (HFCs), cyclopentane and CO_2, it was found that the HFEs investigated show lower thermal conductivities than other promising candidates for the traditional blowing agents for polyurethane foams.

Keywords: Hydrofluoroether; Thermal conductivity; Blowing agent; Steady-state coaxial cylinder

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1. Introduction

Because of the low thermal conductivity, CFC-11 (CCl_3F) had been widely used as the blowing agent for polyurethane foams which show excellent thermal insulating performance for refrigerators. It is common understanding that CFC-11 was phased out because of its high ozone layer depletion potential (ODP). Furthermore, the alternative blowing agent, HCFC-141b (CCl_2FCH_3), is currently not considered as a long-term substitute because of its ODP and its relatively high value of global warming potential (GWP).

There are two kinds of promising substitutes, at present, for these restricted blowing agents. The first one is hydrocarbons (HCs), such as cyclopentane. From an environmental point of view, they are safe materials, but their thermal conductivities are in general too high to use for insulating purposes and this leads to a lower efficiency in refrigerating. The other candidates, hydrofluorocarbons (HFCs), possess relatively lower thermal conductivities, but their GWPs are not always within the acceptable limit. Thus, the development of new alternative substances with both shorter lifetimes and lower thermal conductivities is greatly required. Viewed in this light, we have focused on hydrofluoroethers (HFEs) as the optimum alternative. The lifetimes of the present HFEs with more than one proton are less than seven years [1–5], and it was found that they are shorter than nonflammable HFCs, such as HFC-245fa($CF_3CH_2CHF_2$), HFC-134a-(CF_3CH_2F).

Accurate measurements of gaseous thermal conductivity are extremely difficult [6]. Scattering of data beyond 10% is frequently reported among different authors [7]. In this study, the gaseous thermal conductivities of HFEs were measured by a steady-state coaxial-cylinder method (static method), and the experimental values were compared to the results obtained by a transient hot-wire technique (dynamic method) [8–10].

2. Experimental

2.1. Reagents

The synthesis methods for HFEs investigated in this work are listed in Table 1. These samples were purified by distillation and dried over anhydrous Na_2SO_4 or over molecular sieves 4A. The purities determined with a gas chromatograph (Shimazu GC-14A, Column: PoraPLOT Q (PLOT Fused Silica column) 0.32 mm$\phi \times$25 m) were higher than 99%.

2.2. Measurements by a static method [11,12]

Principle of the static method adopted in this work is schematically illustrated in Fig. 1. A calorimeter (Setaram, C-

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Table 1
Example of synthesis method

No.	Sample	b.p. (°C)	Example	Reference
1	$(CF_3)_3C\text{-}O\text{-}CH_2CH_3$	67.12	$(CF_3)_3CONa + (EtO)_2SO_2$	[29]
2	$(CF_3)_3C\text{-}O\text{-}CH_3$	53.64	$(CF_3)_3CONa + (MeO)_2SO_2$	[29]
3	$CHF_2CF_2\text{-}O\text{-}CH_2CF_3$	56.22	$CF_2 = CF_2 + CF_3CH_2OH + KOH$	[30]
4	$(CF_3)_2CH\text{-}O\text{-}CH_3$	50.95	$(CF_3)_2CHOH + (MeO)_2SO_2 + KOH$	[31]
5	$CF_3CF_2\text{-}O\text{-}CF_2CHF_2$	22.00	$CF_3CF_2OCF_2CClF_2 + H_2$	[32]
6	$CF_3CF_2CF_2\text{-}O\text{-}CH_3$	34.18	$CF_3CF_2COF + (MeO)_2SO_2 + KF$	[33]
7	$CF_3CF_2CH_2\text{-}O\text{-}CHF_2$	45.94	$CF_3CF_2CH_2OH + CHClF_2 + KOH$	[30]
8	$(CF_3)_2CF\text{-}O\text{-}CH_3$	29.35	$CF_3COCF_3 + (MeO)_2SO_2 + KF$	[34]
9	$CH_2FCF_2\text{-}O\text{-}CHF_2$	43.05	$CHClFCF_2OCHF_2 + H_2$	[30]
10	$CHF_2CF_2\text{-}O\text{-}CH_3$	37.19	$CF_2 = CF_2 + CF_3OH + KOH$	[30]
11	$CF_3CHF\text{-}O\text{-}CF_3$	−9.55	$CF_3OCF = CF_2 + HF$	[35]
12	$(CF_3)_2CH\text{-}O\text{-}CHF_2$	42.12	$(CF_3)_2CHOH + CHClF_2 + KOH$	[30]
13	$CHF_2\text{-}O\text{-}CHF_2$	5.16	$CHCl_2OCHCl_2 + HF$	
14	$CF_3CH_2\text{-}O\text{-}CHF_2$	29.00	$CF_3CH_2OH + CHClF_2 + KOH$	[30]
15	$CF_3CF_2\text{-}O\text{-}CH_3$	5.59	$CF_3COF + (MeO)_2SO_2$	[36]

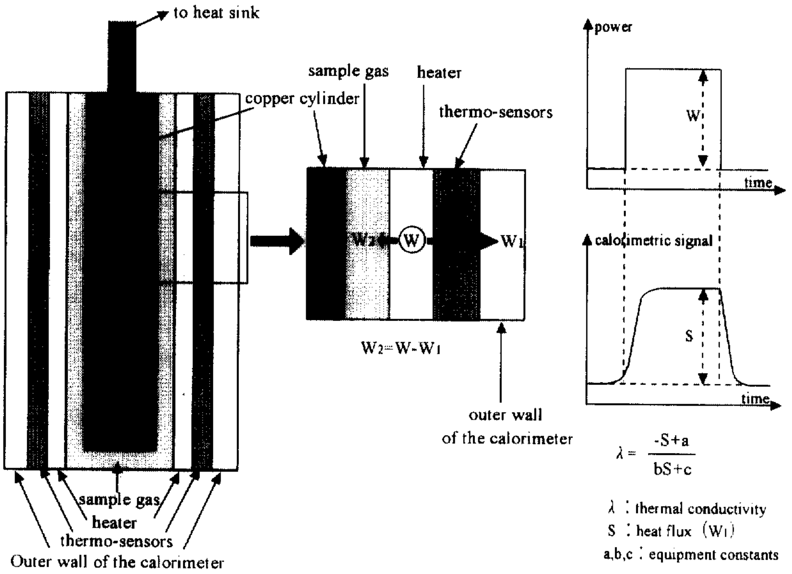

Fig. 1. Principle of the static method.

80D) has more than 200 thermo-piles as a heat sensor (heat flux transducers). The heat energy (w) generated by the heating coil flows both through the annular sample fluid layer to the inner copper cylinder (w_2) and through the heat sensor to the inner copper cylinder (w_1). The heat balance in these processes are dependent upon the thermal conductivities of sample fluid and heat sensor. The heat sensor measures the heat flux to the outer wall of the calorimeter which does not flow to the inner copper cylinder.

After being flushed with sample gas twice, the co-axial cylinder cell, which was heated up to the measuring temperature (50°C or 70°C), was filled up with a sample gas. After the cell reached the thermal equilibrium, a constant energy (100 mW) was supplied to the heater for 1 h. The detected heat flux was converted into the thermal conductivity using the following empirical equation.

$$\lambda=(-S+a)/(bS+c) \qquad (1)$$

where: λ = thermal conductivity (mW/m K); S = detected heat flux (μV); a, b, c = equipment constants.

In this study, measurements were performed on a relative basis. The equipment constants, a, b, and c have been calibrated against seven reference gases (H_2, CH_4, Air, N_2, Ar, CO_2 and CFC-11), whose reference thermal conductivities were collected from reliable data sources [13–19]. The calibration curve at 50°C is shown in Fig. 2. The validity of

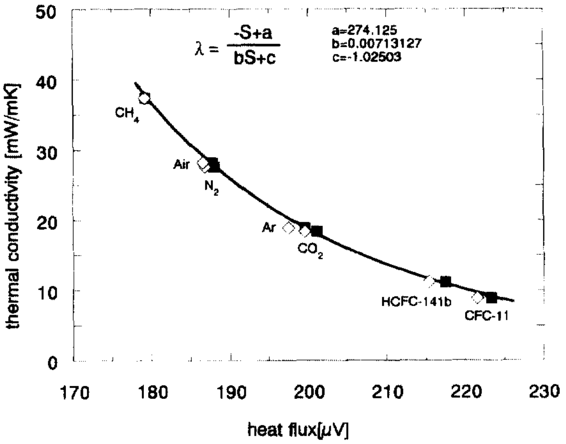

Fig. 2. Calibration curve (static method at 50°C).

calibration curve was examined by HCFC-141b. The gaseous thermal conductivity of HCFC-141b obtained by this work agrees with the result by the transient hot-wire method [20] within 3%. Judging from this result and the reproducibility of measurement, the uncertainty of thermal conductivities obtained was estimated to be less than 4%.

In this work, measurements were usually performed at 50°C. When the boiling points of samples were higher than 45°C, the measurements were performed at 70°C to avoid condensation. In these cases, the data at 70°C were converted into 50°C using the temperature coefficients of thermal conductivities determined by a dynamic method [8].

3. Results and discussion

3.1. Molecular design for blowing agents

The main aim of this research is the development of an efficient and environmentally safe blowing agent. Therefore, the appropriate boiling point is a little lower than 60°C and the carbon numbers of target compounds are less than 6.

Some estimating equations are available for the gaseous thermal conductivity:

$$\lambda = f\eta Cv/M \tag{2}$$

[21–27]

$$\lambda_0 = (15R/4M)\eta_{\text{exptl}} \tag{3}$$

[27]

$$\lambda = (\eta/M)[5/2Cv_{\text{trans}} + (\rho D/\eta)\text{Cv}_{\text{int}}] \tag{4}$$

[28] where η is viscosity, Cv is molar heat capacity, M is molecular weight, ρ is density, and D is self-diffusion coefficient. In each equation, λ (thermal conductivity) is expressed as a reciprocal function of M. This suggests that substances with higher molecular weight are more advantageous in designing new materials with good insulating performance. One of the easiest ways to increase the molecular weight without large elevation in boiling point is the introduction of halogen atoms into the molecule. But the introduction of Cl, Br or I atoms should be avoided to protect the ozone layer. So only the fluorine atom is allowed to be used for this purpose. But excess introduction of fluorine atoms usually makes the life time longer. In this work, therefore,

Table 2
Thermal conductivity of HFEs

No.	Sample	Static method			Dynamic method	Deviation (%)
		Measured temperature (°C)	Thermal conductivity (mW/m K)	Converted value to 50°C[a] (mW/m K)	Measured at 50°C (mW/m K)	
1	$(CF_3)_3C$–O–CH_2CH_3	70.0	13.60[b]	11.85		
2	$(CF_3)_3C$–O–CH_3	70.0	13.75	12.00		
3	CHF_2CF_2–O–CH_2CF_3	70.0	14.11	12.37	12.80	−3.39
4	$(CF_3)_2CH$–O–CH_3	70.0	14.42	12.67		
5	CF_3CF_2–O–CF_2CHF_2	50.0	12.68	12.68	13.3	−2.69
6	$CF_3CF_2CF_2$–O–CH_3	50.0	12.79	12.79	13.09	−2.29
7	$CF_3CF_2CH_2$–O–CHF_2	70.0	14.67	12.93		
8	$(CF_3)_2CF$–O–CH_3	50.0	13.01	13.01		
9	CH_2FCF_2–O–CHF_2	70.0	14.82	13.08	13.46	−2.85
10	CHF_2CF_2–O–CH_3	50.0	13.34	13.34	13.79	−3.26
11	CF_3CHF–O–CF_3	50.0	13.44	13.44	13.70	−1.90
12	$(CF_3)_2CH$–O–CHF_2	70.0	15.20	13.46		
13	CHF_2–O–CHF_2	50.0	13.66	13.66		
14	CF_3CH_2–O–CHF_2	50.0	13.75	13.75	13.88	−0.94
15	CF_3CF_2–O–CH_3	50.0	13.81	13.81	13.94	−0.93
	HFC-254fa	50.0	13.86	13.86		
	cyclopentan	70.0	16.02	14.19		

[a] Converted to 50°C by using dynamic method data when measured at 70°C.
[b] Measured at 0.09 MPa (others at normal pressure).

Table 3
Thermal conductivity of other blowing agent

No.	Blowing agent	b.p. (°C)	Thermal conductivities (mW/m K at 50°C)	Reference
a	CFC-11	23.8	9.61	[19]
b	HCFC-141b	32.0	11.65	[20]
c	CO_2	−78.5	18.66	[18]

the introduction of an ether group has been undertaken and the thermal conductivities of HFEs were measured by a static method.

3.2. Experimental results and comparison with other blowing agents

In this study, 15 kinds of new HFEs were measured by a static method. The experimental data are given in Table 2. Among these HFEs, 9 kinds of HFEs were compared to referential data which were measured by the transient hot-wire technique [3]. Although there was a tendency that the present results determined by the static method showed slightly lower values than the literature values by the dynamic method, the deviations between two methods are less than 3.4%.

Thermal conductivities of some representative blowing agents are given in Table 3. In comparison with the traditional blowing agents, CFC-11 and HCFC-141b, it was found that the present HFEs show considerably higher thermal conductivities. This indicates that the reducing effect on thermal conductivity of the chlorine atoms is quite distinguished. The thermal conductivities are generally arranged in the following order:

$$\mathrm{CFC-11<HCFC-141b<HFEs<HFC-245fa} \\ \mathrm{<cyclopentane<CO_2}$$

It was found that the present HFEs show the lowest thermal conductivities among the promising alternatives.

4. Conclusion

The gaseous thermal conductivities of the HFEs were measured with a reliable static method. It was confirmed that the thermal insulation abilities of HFEs were superior to other promising alternatives. Not only the thermal conductivity but other physical properties should also be considered in the manufacture of efficient polyurethane foams. But as far as the thermal insulating performance is concerned, it can be concluded that the HFEs possess suitable qualities.

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