

Aging of Rigid Polyurethane Foams: Thermal Conductivity of N₂ and Cyclopentane Gas Mixtures

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ABSTRACT: The thermal conductivity of three mixtures of nitrogen and cyclopentane is measured using a transient hot wire method, at temperatures between 315.14 and 395.89 K, and pressures up to 0.53 MPa. These mixtures are important in the evaluation of the evolution of the thermal insulation capacity of closed-cell polyurethane foams considering their aging during the respective applications' total life time. The experimental thermal conductivity data are correlated with the Wassiljewa mixing rules as modified by Mason and Saxena, and predicted using extended corresponding states theory (ECST), with an average absolute deviation of 1.1 and 8.9%, respectively. The increase of the nitrogen fraction in cyclopentane–nitrogen mixtures leads to higher thermal conductivity values than has been predicted by ECST using only pure component thermal conductivity data for all measurements.

KEY WORDS: blowing agents, nitrogen, cyclopentane, thermal conductivity, transient hot wire method.

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INTRODUCTION

Owing to their high thermal insulating capacity, rigid polyurethane (PUR) and polyisocyanurate (PIR) foams are used in a large number of applications, for example, for thermal insulation boards, pipe insulation, technical refrigeration processes, or in the appliance industry. For example, for domestic refrigerators and freezers, PUR foam is the preferred insulating material. This can be explained because self-adhesive rigid foam systems enable a weight-saving sandwich construction to be produced in a single operation. The excellent thermal insulating properties permit a relatively small wall thickness. The insulation capacity of the PUR foam is mainly due to the gases trapped inside the closed cells (blowing agents), that are responsible for 60–65% of the heat transfer through the foam. The effectiveness of a foam blowing agent as an insulator can be characterized by its thermal conductivity in the gas phase relative to the thermal conductivity of air (typically $27 \text{ mW m}^{-1} \text{ K}^{-1}$ at 300 K) that it displaces [1]. Until 1995, CFC-11 was widely used due to its low vapor phase thermal conductivity of $8.3 \text{ mW m}^{-1} \text{ K}^{-1}$ at 300 K [2].

The phaseout of CFC-11 as a foam-blowing agent due to its high ozone depletion potential, as called for under the Montreal Protocol, is well underway. In North America, after having used HCFCs (mostly HCFC-141b) for some years as blowing agents, regulations have led to HFCs (primarily HFC-245fa and HFC-134a) as the preferred approach, since they have zero ozone depletion potential. As compared to hydrocarbons, HFC-245fa has the advantages of a lower gas phase thermal conductivity and of being nonflammable. In Europe, hydrocarbons (mostly cyclopentane and cyclopentane mixtures) have been chosen because of the importance placed on direct emissions of global warming substances [3]. Cyclopentane and cyclopentane mixtures present a zero ozone depletion potential and a much lower global warming potential than HFCs while retaining excellent thermophysical properties for this application. Cyclopentane and cyclopentane mixtures have become the dominant blowing agents in Europe, having taken over nearly 100% of the German market.

As the foam gets older, it loses a considerable part of its thermal efficiency, since due to diffusion into and out of the foam, the composition of the gas in the closed cells is changing with time. Investigations at the Oak Ridge National Laboratory have shown that the thermal conductivity of PUR foam shows an initial rapid increase, which is attributed to diffusion of air into the cells of the foam, followed by a more gradual

increase, which is attributed to diffusion of the blowing agent out of the cells [4].

The kinetics of aging due to diffusion into and out of the foam is dependent on the properties of the foam (e.g., type of isocyanate, type of polyol, cell size, cell openness, blowing agents, initial cell gas composition) and the interactions of cell gases and the gases in the environment with the foam, for example, solubilities and diffusion coefficients. Our investigations are focussed on the thermal conductivity of the cell gas mixture. The results are independent of the properties of the foam. Initially, the cell gas mainly consists of the blowing agent, carbon dioxide, and certain amount of water. With aging, it contains a rising amount of air. Keeping in mind that nitrogen is the more abundant component of air, the study of the thermal conductivity of nitrogen with blowing agent mixtures can give an insight of the efficiency of the aged foam.

In this work, the thermal conductivity of mixtures of nitrogen and cyclopentane was measured using a transient hot wire method, at temperatures between 315.14 and 395.89 K, and pressures up to 0.53 MPa. The obtained results were correlated with the Wassiljewa mixing rule modified by Mason and Saxena. Also, the extended corresponding states theory (ECST) was used to predict the mixture behavior. The ECST was used as it was described in a previous paper [5] with an adjusted proportionality factor, f_{int} , for each pure component.

EXPERIMENTAL

The experimental thermal conductivity measurements were carried out in an apparatus based on the transient hot wire method. Since a detailed description of the apparatus and the technical details are given elsewhere [5–8], only a short description is given here. The measuring cell (stainless steel, 1.4571) consists of two parallel chambers with bare platinum wires of different lengths (ratio of lengths = 0.28) and 10 μm in diameter. The second wire was used to compensate the end effects. The cavity around the hot wires is stainless steel and has a diameter of 16 mm. A schematic view of the apparatus is depicted in Figure 1. The temperature was controlled with an air thermostat within ± 0.1 K. The temperature was measured using calibrated Pt 100 resistance thermometers with an uncertainty within ± 0.1 K, which might lead to an error of $\pm 0.01 \text{ mW m}^{-1} \text{ K}^{-1}$ or 0.06% for the thermal conductivity. The pressure sensors used were transducers from Keller, which were calibrated using a pressure balance (DESRANGES ET HUOT;

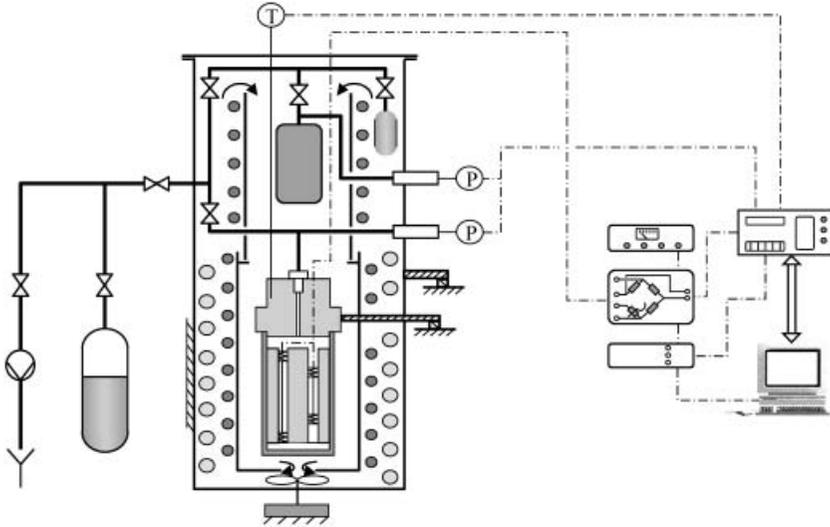


Figure 1. Experimental setup.

Druckblock 410, Type 26000 M, Terminal 20000). The uncertainty of the pressure measurement is within ± 0.1 kPa.

The basic theory behind the transient hot wire method is given by Healy et al. [9]. The essential feature of the transient hot wire method is the precise determination of the transient temperature with a thin metallic wire. This is determined from measurements of the resistance of the wire over a period of a few seconds, followed by the initiation of the heating cycle with a $\Delta T = (2.000 \pm 0.025)$ K. For cylindrical wires with radius r_0 , the ideal temperature rise ΔT on the surface of the wire can be calculated using Equation (1).

$$\Delta T_{\text{id}} = \frac{q}{4\pi\lambda(T_{\text{ref}}, \rho_{\text{ref}})} \ln \frac{4at}{r_0^2 C} \quad (1)$$

where $\lambda(T_{\text{ref}}, \rho_{\text{ref}})$ is the thermal conductivity at the temperature and density reference conditions, a is the thermal diffusivity, $a = \lambda/(\rho C_p)$, q is the heat flow through the wire, t is the time, and $C = \exp(\gamma) = 1.7811 \dots$ is the exponential of Euler's constant γ .

In this work, several corrections to the ideal transient hot wire method were made: corrections due to the finite radius of the wire ($5 \mu\text{m}$) and due to the existence of an outer isothermal boundary layer. In order to give a sufficiently large linear portion to obtain reliable

results for the slope of the temperature rise versus logarithm of time, only the lowest pressure part of the measurements were selected. For each temperature, 40–80 individual data points were taken at different pressures. For the evaluation of the experimental thermal conductivity data, the second virial coefficient and the vapor phase heat capacity of the investigated substances (pure component or mixture) at the temperature and pressure conditions of the experiments had to be known. The pure component virial coefficients were taken from the Bayer thermophysical property database. The vapor phase heat capacity values of nitrogen and of cyclopentane were determined with the Lee–Kesler–Plöcker model [10,11]. The mixture values were calculated by using the arithmetic mean of the pure component values.

The mixtures were prepared before the experiments in a thermostated mixture cell. The temperature was selected to be sufficiently high ($T = 393.15$ K) so that no condensation could occur during the preparation of the mixture. The density of the mixture to be investigated was calculated for the desired mixing pressure and temperature using the Lee–Kesler–Plöcker model [10,11]. Using this information, the filling pressure of the first component (cyclopentane) was calculated. Then, the second component (nitrogen) was carefully added until the desired mixing pressure was reached. The mixture cell was used as a storage container, so that all experiments for a certain composition were performed with the same gas mixture.

Nitrogen was used with no further purification; cyclopentane was degassed by successive melting/freezing cycles while vacuum pumping noncondensable gases.

Before starting the thermal conductivity measurements with the nitrogen and cyclopentane mixtures, the accuracy of the apparatus was checked by measuring the thermal conductivity of the vapor phase of nitrogen at five different temperatures between 315.14 and 395.89 K and at pressures up to 0.514 MPa. An excellent agreement was found between our results and the NIST data [12], with an overall average absolute deviation of 0.6%. The uncertainty at the level of 95% confidence of the experimental data, including the extrapolation to atmospheric pressure, is estimated to be within $\pm 3\%$.

THERMAL CONDUCTIVITY MODELING

Two methods were used to calculate the thermal conductivity of the mixtures measured in this work: the Wassiljewa [13] mixing rules modified by Mason and Saxena [14,15] and the extended corresponding

states theory [16,17]. The gas mixture thermal conductivity, λ_m , using the Wassiljewa mixing rules can be calculated using Equation (2),

$$\lambda_m = \frac{\sum_{i=1}^n y_i \lambda_i}{\sum_{j=1}^n y_j A_{ij}} \quad (2)$$

where n is the number of components of the mixture, λ_i is the thermal conductivity of pure component i , and y_i and y_j are mole fractions of i and j , respectively. The Wassiljewa function, A_{ij} , can be calculated as proposed by Mason and Saxena in Equation (3),

$$A_{ij} = \frac{\varepsilon \left[1 + (\lambda_{tri}/\lambda_{trj})^{1/2} (M_i/M_j)^{1/4} \right]^2}{\left[8(1 + M_i/M_j) \right]^{1/2}} \quad (3)$$

where M is the molecular weight, ε is an adjustable parameter near unity, and λ_{tr} is the monatomic value of the thermal conductivity. The ratio of translational thermal conductivities, $\lambda_{tri}/\lambda_{trj}$, was calculated as proposed by Roy and Thodos [14],

$$\frac{\lambda_{tri}}{\lambda_{trj}} = \Gamma_j \left[\frac{\exp(0.0464T_{ri}) - \exp(-0.2412T_{ri})}{\Gamma_i [\exp(0.0464T_{rj}) - \exp(-0.2412T_{rj})]} \right] \quad (4)$$

where T_r is the reduced temperature and Γ is given by Equation (5).

$$\Gamma = 210 \left(\frac{T_c M^3}{P_c^4} \right)^{1/6} \quad (5)$$

The thermal conductivity was also predicted using the ECST according to the formalism of Ely and Hanley [16], where the thermal conductivity is considered to be a summation of two terms: one arising from the transfer of energy due to translational effects, λ^{trans} , and the other due to the internal degrees of freedom, λ^{int} . Thus,

$$\lambda(\rho, T) = \lambda^{\text{trans}}(\rho, T) + \lambda^{\text{int}}(T) \quad (6)$$

The contribution to λ^{trans} is expressed as a sum of a low-density contribution, λ^* , and a density-dependent contribution, λ^+ ,

$$\lambda^{\text{trans}}(\rho, T) = \lambda^*(T) + \lambda^+(\rho, T) \quad (7)$$

The exact equations to calculate these contributions have been derived before [16,17]. It was observed that the density-dependent translational contribution, $\lambda^+(\rho, T)$, is almost negligible for the thermal conductivity of low pressure gases (below few tenths of a percent), and the shape factors could be set to unity. The term $\lambda^{\text{int}}(T)$ has the dominating role in the thermal conductivity value of low-pressure gases. It is usually calculated using the modified Eucken correction for polyatomic gases [18]

$$\lambda^{\text{int}} = \frac{f_{\text{int}}\eta^*}{M} \left(C_p^{\text{id}} - \frac{5R}{2} \right) \quad (8)$$

where η^* is the dilute-gas viscosity, which can be estimated from kinetic theory, C_p^{id} the constant pressure ideal gas heat capacity, R the universal gas constant, and f_{int} a proportionality factor. In this work, C_p^{id} was calculated using Joback's group contribution method [14]. The f_{int} was used as an adjustable parameter, and it was fitted to experimental pure fluid thermal conductivity data.

RESULTS

Three different mixtures of nitrogen with cyclopentane were prepared: Mixture A, 75.5% of nitrogen with 24.5% of cyclopentane (mole/mole), Mixture B, 50.0% of nitrogen with 50.0% of cyclopentane (mole/mole), and Mixture C, 25.9% of nitrogen with 74.1% of cyclopentane (mole/mole). The pressure dependence of the thermal conductivity for each mixture at each temperature is presented in Tables 1–3 and shown in Figures 2–4. The usual behavior of gas phase thermal conductivity at variations of pressure and temperature [14], that is an increase of the thermal conductivity with pressure and with temperature, was observed.

The thermal conductivity performance of PUR cell gas is usually compared at a pressure of 0.1013 MPa. Therefore, it is a standard procedure to fit the isothermal data to a linear correlation to find the thermal conductivity at 0.1013 MPa. These data were correlated with a simple linear equation

$$\lambda = a^{(1)}P + a^{(0)} \quad (9)$$

where P is the pressure in MPa and λ is in $\text{mW m}^{-1} \text{K}^{-1}$, where $a^{(1)}$ and $a^{(0)}$ are the coefficients of the linear equation. The temperature

Table 1. Vapor phase thermal conductivity of mixture A, 75.5% of nitrogen and 24.5% of cyclopentane (mole/mole), from 315.14 K to 374.56 K; data points at 0.1013 MPa are extrapolated values.

$T = 315.14 \text{ K}$		$T = 354.95 \text{ K}$		$T = 374.56 \text{ K}$	
P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)
0.1013	20.84	0.1013	24.30	0.1013	25.96
0.1040	20.87	0.1089	24.29	0.1095	25.84
0.1040	20.85	0.1089	24.26	0.1097	25.98
0.1040	20.89	0.1089	24.36	0.1097	26.07
0.1041	20.80	0.1089	24.30	0.1097	26.05
0.1041	20.81	0.1089	24.33	0.1097	25.94
0.1042	20.81	0.1089	24.33	0.1098	25.95
0.1042	20.86	0.1090	24.37	0.1098	25.92
0.1042	20.84	0.1090	24.30	0.1098	25.93
0.1043	20.80	0.1090	24.30	0.1974	25.98
0.1504	20.90	0.1090	24.33	0.1975	26.09
0.1504	20.96	0.2128	24.43	0.1975	26.07
0.1505	20.99	0.2128	24.42	0.1975	25.83
0.1505	21.01	0.2129	24.30	0.1976	26.14
0.1505	20.86	0.2129	24.43	0.1976	25.81
0.1505	20.90	0.2129	24.35	0.1976	26.09
0.1505	20.91	0.2129	24.41	0.1976	25.86
0.1505	20.87	0.2129	24.36	0.1977	25.95
0.1505	20.92	0.2130	24.24	0.2854	26.02
0.1982	21.02	0.2130	24.37	0.2854	26.12
0.1982	21.05	0.2130	24.39	0.2855	26.01
0.1982	20.98	0.2130	24.41	0.2855	26.11
0.1983	20.91	0.2130	24.32	0.2856	25.98
0.1983	20.95	0.2130	24.48	0.2856	26.15
0.1983	20.95	0.3105	24.60	0.2857	26.09
0.1983	20.91	0.3105	24.58	0.2857	26.05
0.1983	20.93	0.3106	24.60	0.2857	26.10
0.1983	20.99	0.3106	24.52	0.2858	26.01
0.1984	20.94	0.3106	24.52	0.4023	26.03
		0.3106	24.62	0.4024	26.13
		0.3107	24.52	0.4024	26.00
		0.3107	24.55	0.4024	26.20
		0.3107	24.46	0.4024	26.10
		0.3108	24.48	0.4024	26.14
		0.4125	24.54	0.4024	26.13
		0.4126	24.57	0.4024	26.08
		0.4127	24.60	0.4024	26.08
		0.4128	24.61	0.4025	26.18
		0.4128	24.61	0.5136	26.05
		0.4129	24.59	0.5137	26.05

(continued)

Table 1. Continued.

$T=315.14\text{ K}$		$T=354.95\text{ K}$		$T=374.56\text{ K}$	
P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)
		0.4130	24.60	0.5138	26.06
		0.4131	24.75	0.5139	26.11
		0.4131	24.60	0.5140	26.19
		0.4132	24.73	0.5140	26.13
		0.4954	24.64	0.5140	26.20
		0.4957	24.63	0.5140	26.05
		0.4959	24.79		
		0.4960	24.65		
		0.4963	24.76		
		0.4964	24.64		
		0.4964	24.64		

Table 2. Vapor phase thermal conductivity of mixture B, 50.0% of nitrogen and 50.0% of cyclopentane (mole/mole), from 335.32 K to 375.22 K; data points at 0.1013 MPa are extrapolated values.

$T=335.32\text{ K}$		$T=355.65\text{ K}$		$T=375.22\text{ K}$	
P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1}\text{ K}^{-1}$)
0.1013	19.18	0.1013	20.93	0.1013	22.77
0.1041	19.17	0.1014	20.90	0.1025	22.82
0.1042	19.25	0.1015	20.84	0.1025	22.83
0.1042	19.16	0.1016	20.85	0.1026	22.77
0.1044	19.13	0.1018	20.99	0.1026	22.76
0.1046	19.19	0.1019	20.87	0.1026	22.80
0.1046	19.09	0.1020	20.84	0.1026	22.72
0.1047	19.18	0.1021	20.89	0.1026	22.73
0.1048	19.18	0.1023	20.94	0.1026	22.78
0.1048	19.24	0.2017	21.10	0.1026	22.73
0.2135	19.33	0.2017	21.09	0.2028	22.87
0.2135	19.26	0.2018	21.12	0.2028	22.84
0.2137	19.32	0.2018	20.98	0.2028	22.84
0.2137	19.29	0.2018	21.06	0.2029	22.80
0.2138	19.28	0.2018	21.08	0.2029	22.84
0.2139	19.30	0.2018	21.11	0.2031	22.81
0.2141	19.30	0.2018	21.01	0.2031	22.85
0.2142	19.31	0.2018	21.03	0.2032	22.78
0.2519	19.24	0.2018	21.10	0.2032	22.81

(continued)

Table 2. Continued.

$T = 335.32 \text{ K}$		$T = 355.65 \text{ K}$		$T = 375.22 \text{ K}$	
P (MPa)	λ (mW m ⁻¹ K ⁻¹)	P (MPa)	λ (mW m ⁻¹ K ⁻¹)	P (MPa)	λ (mW m ⁻¹ K ⁻¹)
0.2519	19.27	0.2996	21.08	0.3028	22.91
0.2520	19.30	0.2996	21.13	0.3029	22.98
0.2520	19.27	0.2997	21.08	0.3029	22.93
0.2521	19.31	0.2997	21.15	0.3030	22.95
0.2521	19.32	0.2998	21.03	0.3031	22.86
0.2521	19.28	0.2999	21.08	0.3032	22.95
0.2521	19.34	0.2999	21.07	0.3034	22.91
0.2521	19.26	0.2999	21.10	0.3035	22.86
		0.2999	21.09	0.3035	22.93
		0.2999	21.16	0.3037	22.87
		0.2999	21.14	0.4018	22.98
		0.4131	21.19	0.4028	22.85
		0.4133	21.16	0.4028	22.88
		0.4134	21.22	0.4028	22.84
		0.4135	21.17	0.4050	22.93
		0.4137	21.11	0.4051	22.96
		0.4138	21.09	0.4052	22.99
		0.4140	21.19	0.4053	23.06
		0.4143	21.25	0.4055	23.03
				0.4056	22.92
				0.4399	23.09
				0.4400	22.98
				0.4400	22.98
				0.4401	22.91
				0.4401	23.07
				0.4401	22.97
				0.4402	22.96
				0.4402	23.00
				0.4402	23.05

dependence of the thermal conductivity is also represented by a linear equation

$$\lambda = b^{(1)}T + b^{(0)} \quad (10)$$

where T is the temperature in K, $b^{(1)}$ and $b^{(0)}$ are the coefficients.

The experimental coefficients of the pressure and temperature dependence, from Equations (9) and (10), for each one of the three investigated mixtures are presented in Tables 4–6.

Table 3. Vapor phase thermal conductivity of mixture C, 25.9% of nitrogen and 74.1% of cyclopentane (mole/mole), from 355.16 K to 395.89 K; data points at 0.1013 MPa are extrapolated values.

$T = 355.16 \text{ K}$		$T = 375.94 \text{ K}$		$T = 395.89 \text{ K}$	
P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)
0.1013	18.76	0.1013	21.11	0.1013	23.11
0.1061	18.79	0.1071	21.16	0.1143	23.00
0.1062	18.76	0.1071	21.13	0.1145	23.04
0.1063	18.73	0.1072	21.13	0.1148	23.06
0.1065	18.76	0.1072	21.17	0.1149	23.09
0.1066	18.75	0.1074	21.08	0.1149	22.89
0.1067	18.78	0.1074	21.14	0.1151	22.91
0.1734	18.75	0.1074	21.11	0.1152	23.22
0.1735	18.76	0.1075	21.20	0.1153	23.27
0.1735	18.79	0.1075	21.15	0.2072	23.37
0.1737	18.77	0.1964	21.21	0.2073	23.26
0.1738	18.81	0.1965	21.17	0.2074	23.30
0.1739	18.82	0.1965	21.00	0.2076	23.31
0.2790	18.79	0.1966	21.11	0.2078	23.30
0.2795	18.83	0.1967	21.09	0.2079	23.27
0.2796	18.82	0.1967	21.21	0.2080	23.32
0.2797	18.84	0.1967	21.07	0.2084	23.21
0.2797	18.80	0.1967	21.07	0.2084	23.14
0.2799	18.85	0.1967	21.15	0.3023	23.37
0.2799	18.84	0.1968	21.24	0.3024	23.31
0.2799	18.84	0.2959	21.12	0.3024	23.32
0.2800	18.79	0.2960	21.03	0.3027	23.41
		0.2960	21.12	0.3028	23.32
		0.2960	21.13	0.3029	23.33
		0.2960	21.19	0.3030	23.38
		0.2960	21.11	0.3031	23.27
		0.2960	21.20	0.3033	23.22
		0.2960	21.19	0.3033	23.37
		0.2960	21.19	0.3034	23.36
		0.2961	21.16	0.4054	23.41
		0.3712	21.04	0.4055	23.41
		0.3714	21.07	0.4056	23.34
		0.3714	21.21	0.4057	23.37
		0.3714	21.20	0.4059	23.41
		0.3715	21.12	0.4060	23.53
		0.3715	21.12	0.4061	23.38
		0.3716	21.07	0.4062	23.50
		0.3716	21.15	0.4063	23.49
		0.3716	21.11	0.4065	23.31
		0.4370	21.12	0.4678	23.46

(continued)

Table 3. Continued.

$T = 355.16 \text{ K}$		$T = 375.94 \text{ K}$		$T = 395.89 \text{ K}$	
P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)	P (MPa)	λ ($\text{mW m}^{-1} \text{ K}^{-1}$)
		0.4372	21.29	0.4681	23.46
		0.4374	21.17	0.4684	23.32
		0.4376	21.33	0.4687	23.46
		0.4379	21.20	0.4690	23.48
		0.4381	21.40	0.4691	23.34
		0.4388	21.32	0.4692	23.42
		0.4390	21.42	0.4692	23.44
		0.4394	21.39	0.4692	23.50

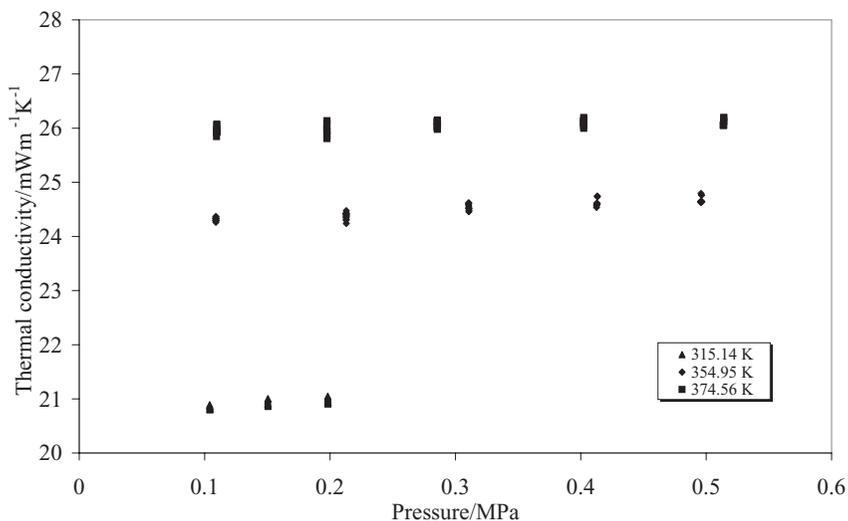


Figure 2. Pressure dependence of the thermal conductivity of mixture A, 75.5% of nitrogen and 24.5% of cyclopentane (mole/mole), at temperatures between 315.14 and 374.56 K.

The linear temperature dependence of the experimental thermal conductivity at 0.1 MPa of the three mixtures are compared with the thermal conductivity of nitrogen and cyclopentane in Figure 5. The dew point curve, below which the mixture of nitrogen and cyclopentane is no longer homogeneous in the vapor phase, is also depicted in Figure 5. The linear equation correlates very well the temperature dependence of the thermal conductivity of the mixtures and of the pure components.

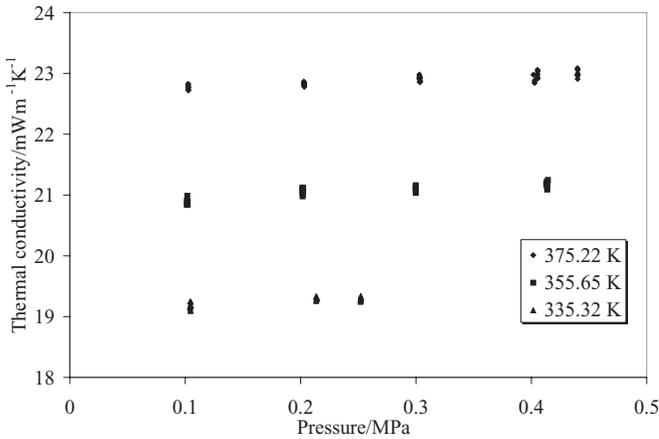


Figure 3. Pressure dependence of the thermal conductivity of mixture B, 50.0% of nitrogen and 50.0% of cyclopentane (mole/mole), at temperatures between 335.32 and 375.22 K.

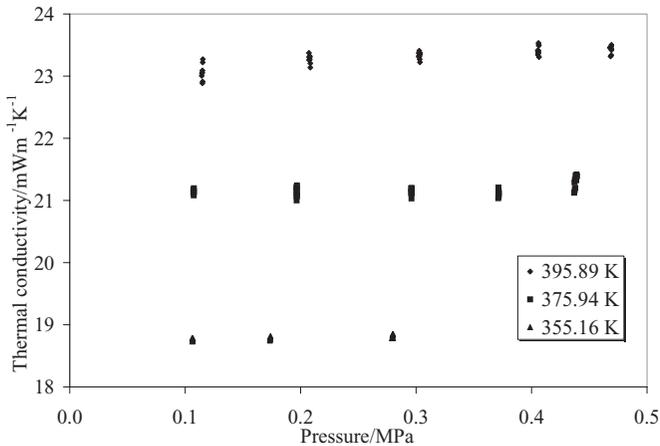


Figure 4. Pressure dependence of the thermal conductivity of mixture C, 25.9% of nitrogen and 74.1% of cyclopentane (mole/mole), at temperatures between 355.16 and 395.89 K.

Figure 6 shows the thermal conductivity of each one of the investigated mixtures as function of the mole fraction of nitrogen, at 313.15, 353.15, and 393.15 K and at 0.1013 MPa. The thermal conductivity of the mixtures was correlated with the modified

Table 4. Pressure and temperature dependence of the thermal conductivity of the mixture A, 75.5% of nitrogen and 24.5% of cyclopentane (mole/mole).

a(1)	a(0)	Temperature (K)
Pressure dependence, Equation (9)		
1.307	20.711	315.14
1.016	24.194	354.95
0.4135	25.920	374.56
b(1)	b(0)	Pressure (MPa)
Temperature dependence, Equation (10)		
0.08625	-6.336	0.1

Table 5. Pressure and temperature dependence of the thermal conductivity of mixture B, 50.0% of nitrogen and 50.0% of cyclopentane (mole/mole).

a(1)	a(0)	Temperature (K)
Pressure dependence, Equation (9)		
0.830	19.095	335.32
0.832	20.850	355.66
0.6527	22.701	375.30
b(1)	b(0)	Pressure (MPa)
Temperature dependence, Equation (10)		
0.08982	-10.96	0.1

Table 6. Pressure and temperature dependence of the thermal conductivity of mixture C, 25.9% of nitrogen and 74.1% of cyclopentane (mole/mole).

a(1)	a(0)	Temperature (K)
Pressure dependence, Equation (9)		
0.3620	18.722	355.16
0.3251	21.074	375.94
0.9627	23.017	395.90
b(1)	b(0)	Pressure (MPa)
Temperature dependence, Equation (10)		
0.1069	-19.16	0.1

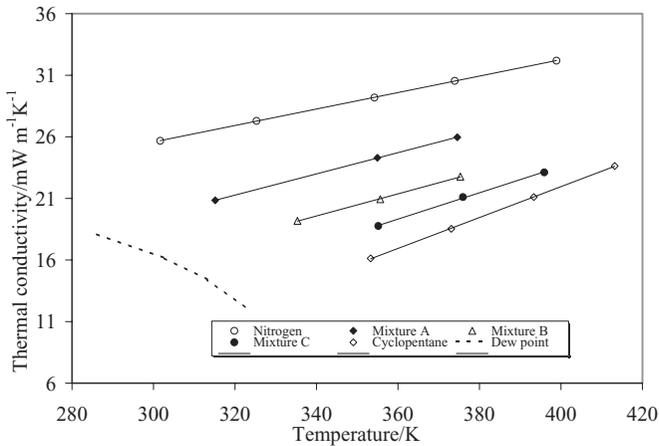


Figure 5. Temperature dependence of the thermal conductivity at 0.1 MPa of nitrogen, cyclopentane, mixture A, mixture B, and mixture C.

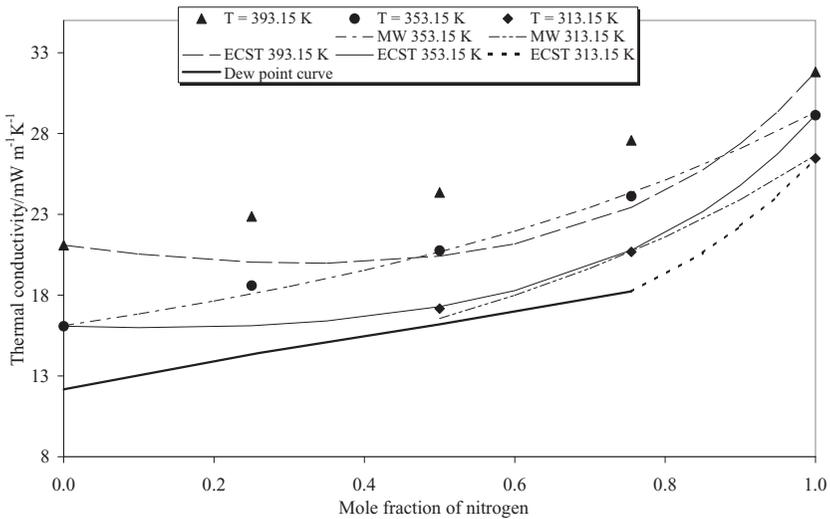


Figure 6. Composition dependence of the vapor phase thermal conductivity of mixtures of nitrogen and cyclopentane. Comparison of the thermal conductivity at 0.1013 MPa with the modified Wassiljewa mixing rules and with ECST.

Wassiljewa mixing rule, with an overall absolute average deviation (AAD) of 1.1%, with one adjustable parameter, $\varepsilon = 0.8923$. The experimental results obtained were predicted with ECST with an overall AAD of 8.9%. The proportionality factor, f_{int} , for each component, adjusted to the experimental thermal conductivity data of

Table 7. ECST adjustable proportionality factor for nitrogen and cyclopentane.

Temperature (K)	Component	
	Nitrogen	Cyclopentane
313.15	0.1108	0.1083
353.15	0.1155	0.1170
393.15	0.1206	0.1257

the pure components is presented in Table 7. Note that ECST predicts too small values for the thermal conductivity of the three mixtures at all temperatures. These predictions show a thermal conductivity minimum at a certain nitrogen content in the mixture, approximately at 0.35 of mole fraction of nitrogen at 393.15 K and approximately 0.10 at 353.15 K. Figure 6 clearly shows that it is not possible to accurately predict the thermal conductivity of nitrogen and cyclopentane mixtures when only pure fluid component data are used.

CONCLUSIONS

The thermal conductivity of mixtures of nitrogen with cyclopentane were measured using the transient hot wire method at temperatures between 301.95 and 398.92 K and up to 0.514 MPa. The modified Wassiljewa mixing rule was successfully used to correlate the experimental thermal conductivity data, using one adjustable parameter. The thermal conductivity predictions obtained with ECST present lower values for the three working mixtures than the experimental data. This behavior was observed before for other blowing agent mixtures [5]. In addition, these predictions show minima at each temperature, approximately 0.35 and 0.1 mole fraction of nitrogen at 313.15 and 353.15 K, respectively. The fact that the thermal conductivity of these mixtures are being underestimated means that the thermal insulation capacity of the PUR foam using these mixtures as blowing agent is in fact worse, closer to the behavior of air, than what could be expected.

It can be concluded from this work that further investigations need to be done in the development of a predictive model for the vapor phase thermal conductivity. In the meantime, due to the discrepancies between the experimental data and the predictive model, more experimental data on the thermal conductivity of cell gas mixtures (blowing agents, carbon dioxide, nitrogen and oxygen) are needed.

NOMENCLATURE

Greek Symbols

λ = thermal conductivity
 γ = Euler's constant
 ρ = density

Latin Symbols

α = thermal diffusivity
 b = cell radius
 C = heat capacity
 C = constant, $C = \exp(\gamma)$
 P = total pressure
 q = heat flow through the wire
 r = radius of the wire
 T = temperature
 t = time
 ΔT = temperature rise of the wire

Subscripts

0 = designates the surface of the wire
C = critical conditions
id = ideal
P = at constant pressure
r = reduced value
ref = at reference conditions

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