Journal of Thermal Analysis, Vol. 41 (1994) 69-79

EFFECT OF EMPTY SPACES ON THE LATTICE THERMAL CONDUCTIVITY OF POLYETHYLENE WITH DIFFERENT DEGREES OF CRYSTALLINITY

A. H. Awad and S. N. Shargi

Department of Physics, College of Education, University of Basrah, Basrah, Iraq

(Received November 19, 1992; in revised form January 22, 1993)

Abstract

A study is presented of the effect of empty space scattering in the estimation of the lattice thermal conductivity of four samples of polyethylene with different degrees of crystallinity at temperatures between 0.4 and 20 K. This study was performed by considering different values of the empty space fraction. It is found that empty space scattering plays a very important role in the calculation of the lattice thermal conductivity of semicrystalline polymers.

Keywords: empty spaces, polyethylene, polymers, thermal conductivity

Introduction

The lattice thermal conductivity of polyethylene has been investigated experimentally and theoretically by a number of workers [1–5]. A study was recently made by the present authors [6] to compute the lattice thermal conductivity of four samples of polyethylene at different degrees of crystallinity between 0.4 and 20 K by considering both the noncrystalline and crystalline structures. The noncrystalline nature was estimated by using the density fluctuation model proposed by Walton [7], while for the second part the Callaway mode [8] was utilized. It was found that the temperature dependence of the lattice thermal conductivity differs for different degrees of crystallinity, and at low temperatures the lattice thermal conductivity of polyethylene is mainly ascribed to the noncrystalline structure; hence, the scattering of phonons by the empty spaces is largely responsible for this.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The effect of empty spaces on the lattice thermal conductivity of polyethylene has been studied by Saleh and Dubey [9]. The present study therefore comes as a continuation of the earlier studies. Its major purpose is to elucidate the effect of the scattering of phonons by empty spaces in the calculation of the lattice thermal conductivity of four samples of polyethylene at different degrees of crystallinity within the temperature range 0.4–20 K for different empty space fractions. The percentage contribution $\%K_N$ of the noncrystalline structure to the total lattice thermal conductivity of the four samples considered is also reported for different empty space fractions.

Theory

From a consideration of both the crystalline and noncrystalline structure of a semicrystalline polymer, Dubey *et al.* [4, 5] expressed the total lattice thermal conductivity of a semicrystalline polymer as the sum of two contributions:

$$K = K_N + K_C \tag{1}$$

where K_N and K_C are the lattice thermal conductivities relating to the noncrystalline and crystalline structures, respectively. Following the density fluctuation model of Walton [7] and also the earlier work of Dubey *et al.* [4, 5], the contribution K_N due to the noncrystalline structure can be expressed as

$$K_N = K_{BE} + K_{EM} + K_{AP} \tag{2}$$

where the contributions K_{BE}, K_{EM} and K_{AP} relate to those phonons which have frequencies $0<\omega<\omega_1(4\times10^{10}$ Hz), $\omega_1<\omega<\omega_{pt}$ (plateau frequency) and $\omega_{pt}<\omega<\omega_D$ (Dubey frequency), respectively, and can be given by

$$K_{BE} = c\int_0^{T_1/T} (\tau_B^{-1} + \alpha x T + Bx^4T^4)^{-1} F(x)dx \tag{3}$$

$$K_{EM} = c\int_{T_1/T}^{T_2/T} (\alpha x T + Bx^4T^4)^{-1} F(x)dx \tag{4}$$

$$K_{AP} = c\int_{T_2/T}^{\Theta_D/T} \tau_{AP}^{-1} F(x)dx \tag{5}$$

where $c = (K_B/2\pi^2 v)(K_B T/h)^3$, $F(x) = x^4 e^x (e^x-1)^{-2}$, $T_1 = h\omega_l/K_B$, $T_2 = h\omega_{pt}/K_B$, $\alpha = (K_B/h)(P/4v)(1-P)^{-1}$, $\beta = (A_o V_o/v^3)(K_B/h)^4$, $x = h\omega/K_B T$, τ_B^{-1} is the boundary scattering relaxation rate [10], $\alpha x T$ represents the scattering relaxation rate due to empty spaces, $\beta x^4 T^4$ is the relaxation rate relating to Rayleigh scattering [11], v is the phonon velocity, V_o is the volume, A_o is a constant and P is the empty space fraction. At low temperatures, the contribution K_{AP} is negligibly small compared with the contributions K_{BE} and K_{EM}.

Following Dubey *et al.* [4, 5] and using the Callaway [8] model, the contribution K_c from the crystalline structure can be given by

$$K_c = c\int_{T_2/T}^{\Theta_D/T} (\tau_B^{-1} + \tau_{dis}^{-1} + \tau_{pt}^{-1} + \tau_{ph}^{-1})^{-1} F(x)dx \tag{6}$$

where τ_{dis}^{-1}, τ_{pt}^{-1} and τ_{ph}^{-1} are the dislocation [12], point defect [12] and phonon-phonon [13] scattering relaxation rates, respectively, and can be written as $\tau_B^{-1} = v/L$, $\tau_{pt}^{-1} = A\omega^4$, $\tau_{dis}^{-1} = a\omega$ and $\tau_{ph}^{-1} = B\omega^2 T^3$, where L is the Casimir length of the sample [10], ω is the phonos frequency, and A, a and B are the scattering strengths of the respective processes. It should be noted that the contribution of the correction term arising from the three-phonon normal processes to the total lattice thermal conductivity is usually very small [14, 15], and thus its contribution can be neglected.

Results and discussion

The lattice thermal conductivities of the four samples of polyethylene with degrees of crystallinity between 0.43 and 0.81 in the range 0.4–20 K are calculated by means of the parameters illustrated in Table 1, taken from our earlier report [6], which represents a theoretical fit of experimental data obtained from Ref. [2]. All other relevant properties of these samples were determined by Kolouch and Brown [2] and Choy [16]. Different empty space fractions P are selected, such as $P = 0.95$ to 0.2 and $P = 10^{-3}$. The variation in the lattice thermal conductivity is plotted against temperature for the constant empty spaces of the samples considered in Figs 1–4. The dependence of the lattice thermal conductivity upon the empty space fraction at constant temperature (1 K) for the four samples of interest is illustrated in Fig. 5, while the dependence on the degree of crystallinity for constant empty space fractions P is depicted in two distinct groups, one for a temperature of 1 K and the other for 10 K. The percentage contributions arising from the noncrystalline structure of the four samples,

Table 1 Values of the physical parameters used in the study of the lattice thermal conductivity of polyethylene

	X=0.43	X=0.56	X=0.71	X=0.81
T_1/K	0.4	0.4	0.4	0.4
T_2/K	10	10	10	10
θ/K	135	135	135	135
$v/10^5 cm \cdot s^{-1}$	1.98	2.01	2.17	2.26
$\beta/10^7 s^{-1} K^{-1}$	2.8	3.0	3.5	4.0
a	0.115	0.08	0.045	0.02
$A/10^{-40} s^3$	0.77	0.75	0.3	0.08
	1.0	1.0	1.0	1.0
$B/10^{-25} s \cdot K^3$	1.0	1.0	1.0	1.0
P	0.999793	0.999808	0.999822	0.999839

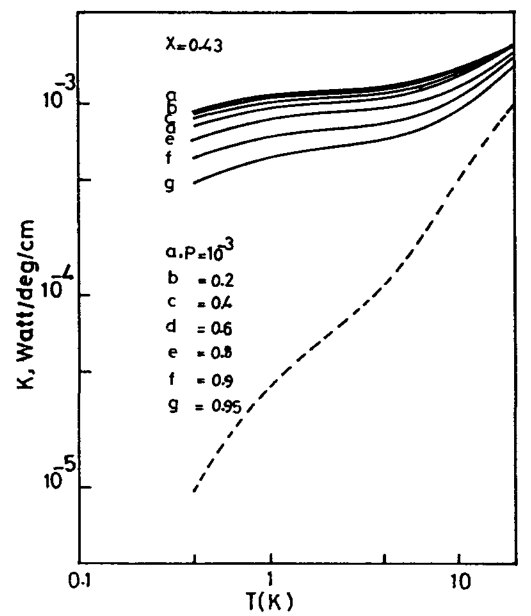

Fig. 1 Lattice thermal conductivity of polyethylene having degree of crystallinity 0.43 for different values of empty space fraction P at temperatures between 0.4 and 20 K. The dotted line is related to P = 0.999793

Table 2 The percentage contribution to the lattice thermal conductivity due to noncrystalline stucture of the four samples for the different values of empty space fraction P

	X=0.43						X=0.56					
	P						P					
T/K	10^{-3}	0.2	0.6	0.8	0.9	*	10^{-3}	0.2	0.6	0.8	0.9	*
0.4	100	100	100	100	100	100	100	100	100	100	100	100
0.6	100	100	100	100	100	100	100	100	100	100	100	100
0.8	100	100	100	100	100	99.98	100	100	100	100	100	99.96
1	99.99	99.99	99.99	99.99	99.99	99.90	99.99	99.99	99.99	99.99	99.98	99.85
2	99.65	99.64	99.61	99.60	95.03	94.64	99.54	99.53	99.51	99.43	99.33	92.03
4	96.83	96.76	96.44	95.87	95.10	65.51	95.22	95.20	94.76	93.95	92.86	55.46
6	91.67	91.49	90.70	89.52	87.64	42.06	88.00	87.84	86.82	85.14	82.71	32.40
8	85.55	85.26	84.01	82.07	79.25	28.40	80.01	79.59	78.02	75.68	72.27	20.95
10	79.19	78.82	77.22	74.71	71.52	20.56	72.31	71.82	69.87	66.96	62.98	14.86
15	65.56	65.04	62.80	59.54	55.16	11.52	57.20	56.62	54.30	50.93	46.56	8.27
20	56.01	55.43	53.04	49.57	45.15	8.03	47.69	46.18	44.84	41.49	37.29	5.82

(*) From Table 1

Table 2 Continued

	X=0.71						X=0.81					
	P						P					
T/K	10^{-3}	0.2	0.6	0.8	0.9	*	10^{-3}	0.2	0.6	0.8	0.9	*
0.4	100	100	100	100	100	100	100	100	100	100	100	100
0.6	100	100	100	100	100	100	100	100	100	100	100	100
0.8	100	100	100	100	100	99.96	100	100	100	100	100	99.91
1	99.98	99.98	99.98	99.98	99.98	99.73	99.97	99.97	99.97	99.96	99.95	99.34
2	99.14	99.12	99.04	98.91	98.70	85.79	97.90	97.68	97.60	97.37	96.90	70.96
4	90.92	90.76	90.01	88.80	86.99	39.10	80.10	79.79	78.45	76.29	73.17	20.47
6	78.49	78.15	76.66	74.27	70.91	19.66	59.32	58.78	56.79	53.75	49.66	8.86
8	66.25	65.80	63.85	60.83	56.73	11.80	43.53	43.06	41.11	38.18	34.39	4.99
10	55.87	55.38	53.26	50.06	45.85	8.01	32.89	32.49	30.74	28.21	25.01	3.26
15	38.66	38.19	36.20	33.30	29.68	4.19	19.06	18.88	17.58	15.88	13.82	1.60
20	29.64	29.23	27.50	25.03	22.00	2.85	13.27	13.06	12.17	10.92	9.43	1.05

(*) From Table 1

%K_N, to the lattice thermal conductivity for different empty space fractions are listed in Table 2.

Figures 1–5 reveal that even a small variation in the empty space fraction may cause a significant variation in the lattice thermal conductivity and it is quite clear that at each temperature the lattice thermal conductivity of the polyethylene samples decreases with increase in the empty space fraction. Figures 1–4 also demonstrate that at low temperatures the lattice thermal conductivity increases drastically with decreasing empty space fraction, while it shows a slight increase at high temperatures. This indicates that at low temperatures the scattering of empty spaces by phonons almost predominates over other scattering mechanisms. As concerns the slight variation in lattice thermal conductivity with empty space fraction at high temperatures, it would be instructive to suggest that at low empty space fractions there is an apparent existence of %K_N at this temperature level, leading to a reduction in the percentage contribution due to the crystalline structure %K_C, which predominates.

With the help of Fig. 5, one can see that at high empty space fractions (say above 0.6) the lattice thermal conductivity decreases rapidly with increasing empty space fraction for each sample. Figure 6 illustrates that at low tempera-

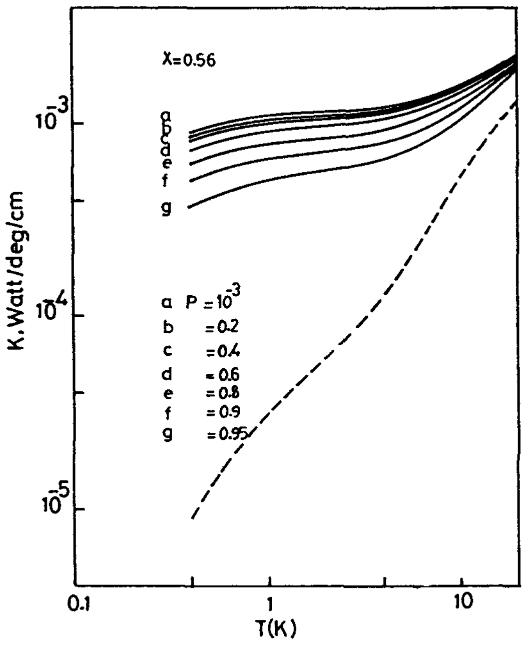

Fig. 2 Lattice thermal conductivity of polyethylene having degree of crystallinity 0.56 for different values of empty space fraction P at temperatures between 0.4 and 20 K. The dotted line is related to P = 0.999808

ture (1 K), for each empty space fraction, the lattice thermal conductivity decreases as the degree of crystallinity increases, while at a somewhat higher temperature (10 K) it shows an opposite trend, increasing with increasing degree of crystallinity. This contrasting behaviour of the lattice thermal conductivity as the temperature of the sample is varied from 1 to 10 K is clear from Table 2. It seems that for any value of empty space fraction P the percentage contribution from the noncrystalline structure, $\%K_N$, to the lattice thermal conductivity at low temperatures becomes dominant and then decreases as the degree of crystallinity increases, while it decreases with increasing temperature. Therefore, the percentage contribution due to the crystalline structure, $\%K_C$, predominates over $\%K_N$. This $\%K_C$ in turn increases with increasing degree of crystallinity, which is in agreement with our previous finding [6].

Table 2 also demonstrates a decrease in the percentage contribution of the noncrystalline structure, $\%K_N$, with increase in the empty space fraction, which means that an increase in the empty space scattering gives rise to a K_N decrease, whereas K_C remains unchanged. Therefore, $\%K_N$ appears to decrease as the empty space fraction increases. This Table also shows that any small change in the empty space fraction may influence $\%K_N$, which occurs even at high temperatures (say 20 K). The effect of variation in the empty space fraction on the

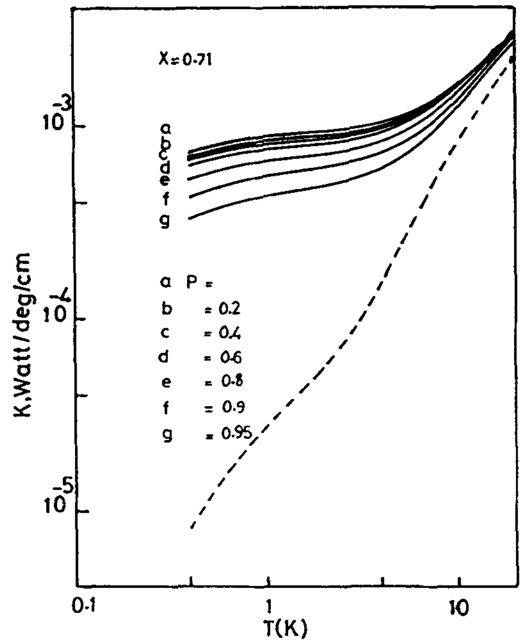

Fig. 3 Lattice thermal conductivity of polyethylene having degree of crystallinity 0.71 for different values of empty space fraction P at temperatures between 0.4 and 20 K. The dotted line is related to P = 0.999822

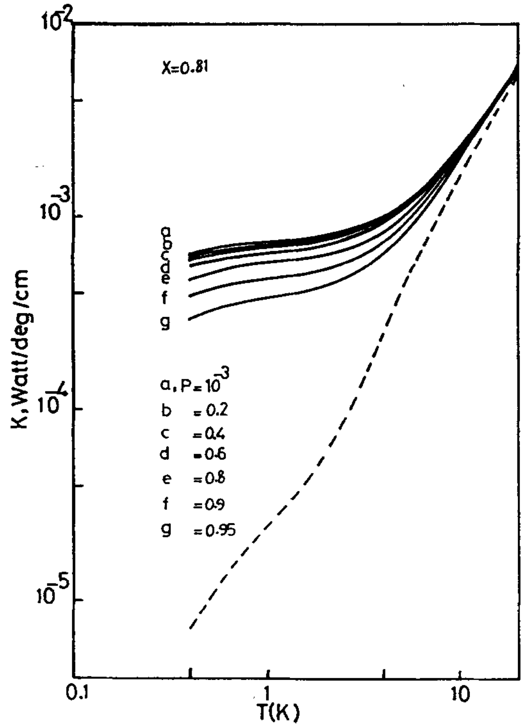

Fig. 4 Lattice thermal conductivity of polyethylene having degree of crystallinity 0.81 for different values of empty space fraction P at temperatures between 0.4 and 20 K. The dotted line is related to P = 0.999839

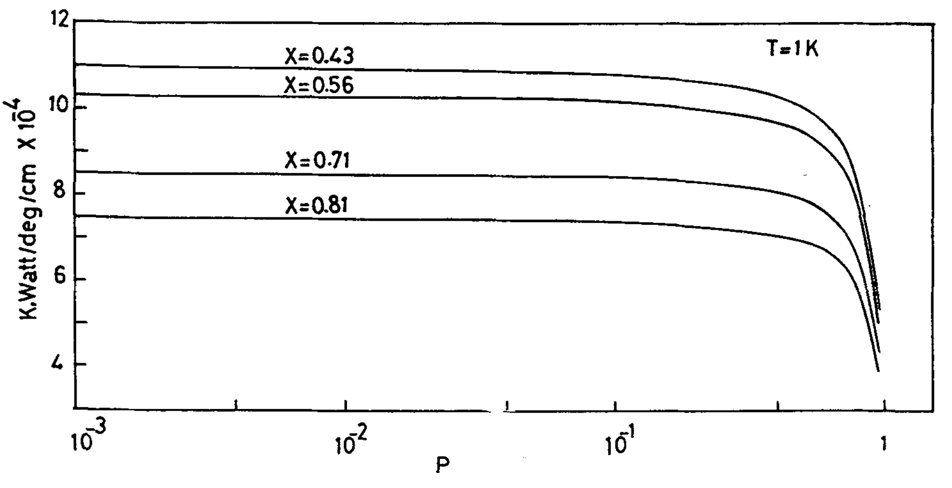

Fig. 5 The variation of the lattice thermal conductivity with empty space fraction P at constant temperature for different degrees of crystallinity X

lattice thermal conductivity becomes evident. Finally, the data show that any small empty space fraction does not change the inverse proportion between the lattice thermal conductivity and the degree of crystallinity at 1 K.

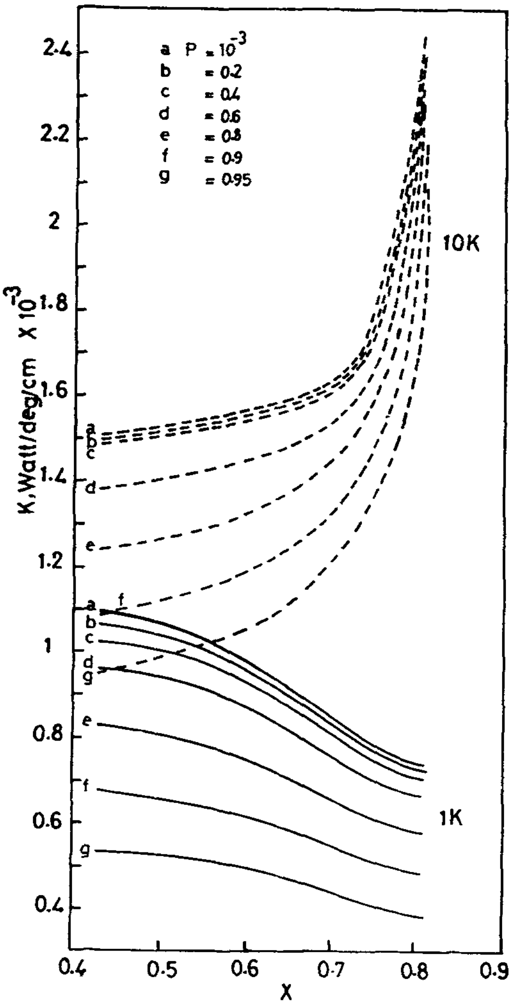

Fig. 6 The variation of the lattice thermal conductivity with degree of crystallinity X at constant temperatures (1 and 10 K) for different values of empty space fraction P

References

1 T. A. Scott, J. D. Bruin, M. M. Giles and C. Terry, J. Appl. Phys., 44 (1973) 4212.
2 R. J. Kolouch and R. G. Brown, J. Appl. Phys., 39 (1968) 3999.
3 D. S. Dubey, Solid State Commun., 15 (1974) 875.
4 A. F. Saleh, R. H. Misho and K. S. Dubey, Acta Phys. Acad. Sci. Hungarica, 50 (1981) 321.
5 A. F. Saleh and K. S. Dubey, Ind. J. Pure and Appl. Phys., 19 (1981) 73.
6 A. H. Awad and S. N. Shargi, J. Thermal Anal., (to be published).
7 D. Walton, Solid State Commun., 14 (1974) 335.
8 J. Callaway, Phys. Rev., 113 (1959) 1046.
9 A. F. Saleh and K. S. Dubey, Acta Physica Polonica, A58 (1980) 521.
10 H. B. G. Casimir, Physica, 5 (1938) 495.
11 Lord Rayleigh, Theory of Sound, Vol. 2, McMillan & Co., London (1878).
12 P. G. Klemens, Solid State Physics, 7 (1958) 1.
13 C. Herring, Phys. Rev., 95 (1954) 954.
14 A. H. Awad, Acta Physica Hungarica, 67 (1–2) (1990) 211.
15 K. S. Dubey, Phys. Stat. Solidi, (b) 79 (1977) K119.
16 C. L. Choy, Polymer, 18 (1977) 984.

Zusammenfassung — Es wird eine Untersuchung des Einflusses von Freiraumstreuung bei der Schätzung der thermischen Gitterleitfähigkeit von vier Polyethylenproben mit verschiedenem Kristallinitätsgrad im Temperaturbereich zwischen 0.4 und 20 K dargelegt. Diese Untersuchung wurde unter Inbetrachtnahme verschiedener Werte von Freiraumstreuung durchgeführt. Man fand, daß Freiraumstreuung bei der Berechnung der thermischen Gitterleitfähigkeit von semikristallinen Polymeren eine wichtige Rolle spielt.