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Analysis of Lattice Thermal Conductivity of Amorphous Polymer at low Temperatures

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Abstract

The lattice thermal conductivity (K) of amorphous polymer at low temperatures has been analyzed by expressing its total lattice thermal conductivity as a sum of the three contributions as $K=K_{BE}+K_{EM}+K_{AP,}$ Where K_{BE} is the contribution due to those phonons is can interact with crystal boundaries, K_{EM} is due to those phonons which have frequencies less than the plateau frequency (w_{pt}) and K_{AP} is due to those phonons which have frequencies larger that (w_{pt}). the study had been made for polymethyl mathacrylat in the temperature range 0.1- 4K within the frame work of the expression proposed by Saleh *et al.* which has base on Walton's theory. A very good agreement has been obtained between experiential and calculated values of K at low temperatures. It has also been found that at low temperatures, the total K of a non crystalline is mainly due the contribution K_{EM} which is due to empty spaces.

Keywords: Thermal Conductivity, amorphous polymer, Phonons, Contributions.

1. Introduction

The transport properties of the amorphous polymer have received sufficient attention recently because of their vast applications in present day technology. Recent studies[1-2] on a number of amorphous polymers have well established the fact that the temperature dependence of the lattice thermal conductivity (K) of a noncrystalline polymer is almost similar to that of inorganic noncrystalline [3] material it is also clear that at very low temperatures (say below 1K), K of an amorphous polymer is approximately proportional to T^2 and as temperature rises, K increases more slowly until it becomes nearly independent of the temperature, in a particular range (say 10-15k) which is known as plateau region. At higher temperatures, K again shows increasing trend with temperatures and above a certain temperature, K becomes proportional to the specific heat; it should also be noted that the measurements show that K of a noncrystalline polymer depends little on its chemical composition.

It was klemens [4], who first gave a phenomenological treatment for the calculation of the phonon mean free path (MFP) in a noncrystalline material using the density fluctuation method. He reported that the MFP is proportional to q^2 where q is the phonon wave vector. But q^2- dependence of the MFP could not explain the experimental data for K of an amorphous material. Later, Walton [5] proposed that the empty spaces in an amorphous structure are responsible for the scattering of phonons. Walton's idea was recently incorporated by Sales et al. [6-9] in the calculation of K of some semi crystalline polymers, and it is found that it accounts well for the values of K at low temperatures. The expression derived by Walton [5] for the MFP of phonons due to an empty space fraction has also been used by Dubey [10] recently in the explanation of the K of borosilicate glass at low temperatures.

Experimentally, it is found [11-12] that phonons can propagate in a noncrystalline material at frequencies up to ω_1=4x10^{10} Hz (which corresponds to temperature $T_1 \cong 0.4K$) and hence contribute to the thermal transport. In view of the above stated fact and following the earlier work of Dubey [10], K of a noncrystalline polymer can be analyzed by expression its total K as a sum of the three contributions as $K = K_{BE}+K_{EM}+K_{AP}$, Where K_{BE} is the contribution crystal boundaries; K_{EM} is due to those photons which have frequencies less than the plateau frequency ω_{pt} (frequency corresponding to plateau temperature) and such phonons can interact with empty spaces only; and the contribution K_{AP} is due to those phonons which have frequencies larger than ω_{pt}. The aim of the present work is to analyze data on K of polymethayl methacrylate (PMMA) in the temperature range 0.1-4K by estimating each contribution separately. The variations of the relative contributions due to K_{BE} and K_{EM} towards the total value of K of PMMA with temperature are also reported in the present work to see the domination of one over the other. The variation of the scattering relaxation rates used in the present analysis with the dimensionless parameter x has also been analyzed at a constant temperature for the samples PMMA.

2. Experimental

2.1 Expression for Lattice Thermal Conductivity:

The ultrasonic as well as the light scattering experiments [12-13] show that the phonons can propagate in a noncrystalline material at frequencies up to $\omega_l = 4x\ 10^{10}$ Hz which corresponds to temperature $T_1 \cong 0.4K$. From the earlier report of Anderson and his co-workers [14-15], it is clear that such phonons can interact with the crystal boundaries and hence contribute towards the thermal resistance.

Following the ideas of Klemens [4] and Walton [5], we assume that an amorphous structure has a fraction p of its volume empty and these empty spaces are randomly distributed. As a result these empty spaces are responsible for the scattering of phonons. Following the earlier reports of Walton[5]as well as Saleh et al. [3-5] the MFP of phonons can be expressed as

$$L_1^{-1} = \frac{1\ pq}{4\ l\text{-}p} + Aq^4V_0, \qquad \text{for } qV_0^{\ 1/3} \leq ,\ w \leq w_{pt} \tag{1}$$

$$L_2^{-1} = BV_0^{-1/3}, \qquad \text{for } qV_0^{1/3} > 1,\ w > wpt \tag{2}$$

Where q is the phonons wave vector, A and B are constants, is the critical volume. The first term in Eq.(1) corresponds to the scattering of phonons by empty spaces[6] while the second term corresponds to the Rayleigh scattering[7].

As stated earlier, the phonons having frequencies $w \leq w_1 = 4x10^{10}$ Hz can also interact with the crystal boundaries. Following the earlier work of Dubey [10], using the idea of the boundary scattering [16] and considering Eqs. (1) and (2), the combined scattering relaxation are can be expressed as

$$\tau_{BE}^{-1} = \tau_B^{-1} + \alpha\, x\, T + \beta\, x^4\, T^4 \quad 0 < \omega < \omega_1 \tag{3}$$

$$\tau_{EM}^{-1} = \alpha\, x\, T + \beta\, x^4\, T^4 \qquad \omega_1 < \omega < \omega_{pt} \tag{4}$$

$$\text{and} \qquad \tau_{AP}^{-1} = \beta \qquad \omega_{pt} < \omega < \omega_D \tag{5}$$

Corresponding to three different frequency regions, In Eqs (3)-(5), τ_{BE}^{-1} is the combined scattering relaxations rate due to those phonons which can interact with the crystal boundaries as well as with the empty spaces t^{-1}EM: is the combined scattering relaxation rate due to those Phonons which can interact with the empty space only, and τ_{AP}^{-1} is the combined scattering relaxation rate due to those phonons whose frequencies lie in the range ω_{pt} - ω_D and is independent of temperature: ω_D is the Debye frequency t^{-1}B: is the boundary scattering relaxation rate due to Casimir [17] and is given τ_B^{-1} = V/L, V is the phonon velocity and L is the Casimir length , α β and β' are constants and are given by

$$\alpha = 1/4\ (P/1\text{-}P)\ (K_B/\hbar),\ \beta = A\ /V^3\ (KB/\hbar)^4,$$

$$\text{and} \quad \beta' = BVV_0^{-1/3}$$

Where KB is the Boltzmann constant and h=h/2π, h being the Planck's constant.

Though some refinements [19-20] have been sought to be introduced recently, the Callaway [18] integral has been enormously successful in explaining the experimental data of K at low temperatures. Keeping in view the combined scattering relaxation rate and the frequency ranges as stated in Eqs (3)-(5). Following the earlier work of Dubey[10] and considering the Callaway integral [15], the total K of a noncrystalline polymer can be expressed as a sum of three contributions, as

$$K = K_{BE} + K_{EM} + K_{AP} \tag{6}$$

$$\text{With } K_{BE} = C\int_0^{T_1/T} (\tau_{BE}^{-1})^{-1} x^4 e^x (e^x - 1)^{-2}\, dx \tag{7}$$

$$K_{EM} = C\int_{T_2/T}^{T_1/T} (\tau_{EM}^{-1})^{-1} x^4 e^x (e^x - 1)^{-2}\, dx \tag{8}$$

$$K_{AP} = C\int_{T_2/T}^{\theta/T} (\tau_{AP}^{-1})^{-1} x^4 e^x (e^x - 1)\, dx \tag{9}$$

Where C= $(K_B/\pi^2 V)(K_B T/h)^3$, T_1 is the temperature corresponding to frequency $4\text{x}10^{10}$ Hz, T_2 is the plateau temperature, θ is the Debye temperature and other terms have the same meaning as defined earlier.

It should be noted that at low temperatures. The contribution K_{AP} is negligibly small compared to the contribution K_{BE} and one can neglect its contribution at low temperatures. The total K of the amorphous polymer in the present analysis can thus be expressed as

$$K = C\left[\int_0^{T_1/T} (\tau_{BE}^{-1} + \alpha xT + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2}\, dx + \int_{T_1/T}^{T_2/T} (\alpha xT + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2}\, dx\right] \tag{10}$$

The first integral in Eq. (10) represents K_{BE} while the second integral shows the contribution K_{EM}.

2.2 Lattice Thermal Conductivity of poly methyl Methacrylate (PMMA)

At low temperatures, the phonons are not excited to a large extent, as a result, the lattice thermal resistivity of a sample is mainly due to scattering of phonons by the crystal boundaries. Assuming α and β as zero, as approximate value of τ_B^{-1} has been estimated at 0.1 K knowing an approximate value of τ_B^{-1} , the constants α and β have been estimated at 0.2 and 1K respectively. All the three parameters, viz. τ_B^{-1} α and β have been finally corrected at 0.5k and the value obtained are reported in table-1. The experimental data for k of PMMA of the theoretical analysis in the present work have been taken from the earlier work of Choy et al. [21].

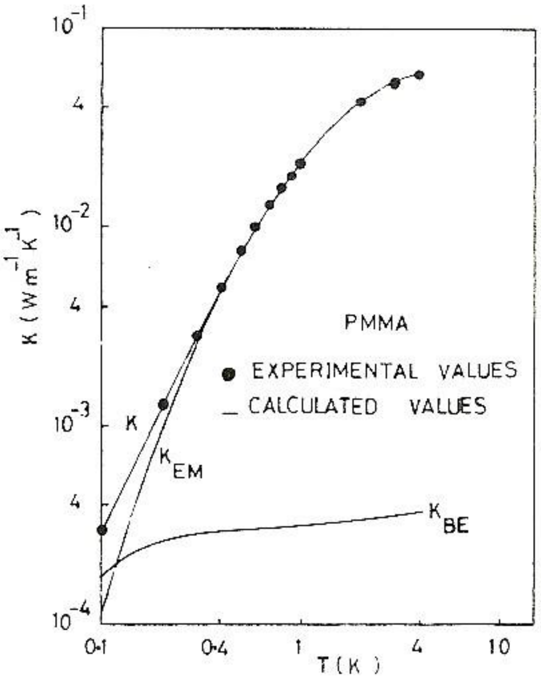

Fig.1. Variation of the calculate K, K_{BE} and K_{EM} with the temperature for PMMA along with the experimental values.

Using the constants reported in the table-1, the total value of k of PMMA has been analyzed in the entire temperature range 0.1-4k by calculating the contributions K_{BE} and K_{EM} separately with the help of the numerical integration of the conductivity integrals stated in Eq.(10) and the results obtained are reported in Fig.1. The percentage contributions due to K_{BE} and K_{EM} towards the total value of K of PMMA have also been analyzed and the results obtained are reported in Fig.2. These results have also been reported in Table-2 to enable a better appreciation of the actual magnitudes.

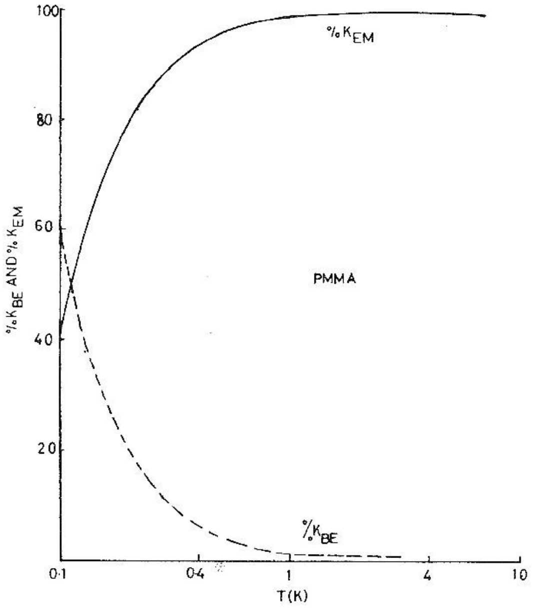

Fig-2: The Contribution % K_{BE} and %K_{EM} for PMMA in the Temperature range 0.1-4K.

The variation of τ_B^{-1} α x T and β x^4 T^4 with the dimensionless parameter x have also been analyzed to see their relatives roles in the estimation of K of PMMA.

3. Results and Discussion

With the help of Figs, 1 and 2, it can be seen that the agreement between the calculated and experimental value of K of PMMA is very good in the entire temperature range 0.1-4 K. which shows that the expression for K used in the present work gives a very good response to K of the amorphous polymer at low temperatures.

From Fig. 1 and 2 and table2, it is clear that, except at very low temperatures, % K_{EM} is much larger than % K_{BE} for both of the samples. As a results, one can say that, at low temperatures, the total value of K for a non crystalline polymer is mainly due to scattering of phonons by empty spaces plays an important role. In other words, it can also be said that the low temperature lattice thermal resistivity of a non crystalline polymer is mainly due to scattering of phonons by empty spaces. Which is similar to the earlier observation of Dubey [1] for borosilicate glass. From Fig.2 it can also be seen that % K_{BE} decreases with temperature and the reverse is true for % K_{EM}. It can also be seen from table-2 that the nature of the variation of % K_{EM} and %K_{BE} for PMMA. It is interesting to note that this nature of variation of % K_{BE} and % K_{EM} reported in the present work for PMMA to that reported by Dubey [1] for borosilicate glass at low temperature.

The variations of τ_B^{-1}, α x T and βx^4T^4 with the dimensionless parameter x at a constants temperature for PMMA, enable us to study the relative role of τ_B^{-1}, α x T and βx^4T^4 in the estimation of the total K of the respective samples. It can be seen that at very low temperature α x T (scattering relation rate due to empty spaces) dominate over βx^4T^4 (Rayleigh scattering) whereas the term βx^4T^4 is larger than α x T for large value of x at higher temperatures (Say 1K). It should also be noted that at very low temperatures and for low values of x, τ_B^{-1} is larger than the other term showing the boundary scattering also.

4. Conclusions: The low temperature lattice thermal resistivity of a non crystalline polymer is mainly due to scattering of phonons by empty spaces, which is similar to the earlier observation for borosilicate glass, which shows that the expression for K used the present work gives a good response to K of the amorphous polymer at low temperatures.

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Table1- Constants and parameters used in the analysis of K of PMMA in the temperature range 0.1-4K. (PMMA)

V (m/sec)	2.7 x 103
T_1 (K)	0.4
T_2 (K)	10
τ_B^{-1} (sec^{-1})	3.4x10^6
α (sec-1 K^{-1})	1.25x10^8
β (sec-1K^{-4})	1.5x10^6

Table 2- Contribution of K_{BE} and K_{EM} towards Total K of PMMA in the temperature range 0.1-4K (PMMA)

T(K)	%K_{BE}	%K_{EM}
0.1	59.9	40.1
0.2	20.51	79.49
0.4	5.93	94.07
0.6	2.99	97.01
0.8	1.94	98.06
1.0	1.44	98.56
2.0	0.76	99.24
3.0	0.64	99.36