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THERMAL PROPERTIES OF PURE AND DOPED (POLYVINYL-ALCOHOL) PVA

M. I. Abdel-Ati[1], *O. M. Hemeda*[1], *M. M. Mosaad*[2] *and D. M. Hemeda*[1]

[1]Physics Department, Faculty of Science, Tanta University, Tanta, Egypt
[2]Physics Department, Faculty of Education, Kafr El-Sheikh, Egypt

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Abstract

Films ≈350 μm of poly(vinyl-alcohol) composites, containing copper (Cu), aluminium (Al) and iron (Fe), metallic powder very fine, were prepared by a casting method. Thermal conductivity, phonon velocity, mean free path and specific heat were studied. The pure sample of PVA has a lower values of thermal conductivity than that which are doped with metals. For all samples the thermal conductivity K increases up to a certain temperature T_{gg} (120–160°C) and then decreases with temperature. The specific heat increase with temperature up to ≈ 120°C and above 120°C is nearly independent on temperature. The pure sample of PVA has small values of mean free path (L)≈ 0.2 Å at room temperature, but for PVA$^+$ metals L≈ 2.0 Å. The phonon velocity of pure PVA is larger than that of PVA containing metals.

Keywords: polymers, thermal conductivity

Introduction

In dielectrics, heat is transferred by thermal vibrations of the lattice. If a temperature gradient exists in a body vibrational quanta of thermal energy, called phonons [1] may be considered to flow along the thermal gradient. The thermal conductivity of the body is determined by inelastic collisions and scatter of the phonons or, in analogy with the kinetic theory, by the mean free path of the phonons. The factors which may affect thermal conductivity in polymers are grain boundaries, pores, impurities, lattice imperfections, and radiation through the material. The effect of impurities was considered by Eucken and Kuhn [2], who observed that single crystals of chemically pure components showed conductivities up to 50% higher than those of impure natural crystals. The theory of thermal conductivities discussed earlier predicts that the conductivity of an ideal dielectric above its Debye temperature, is inversely propor-

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tional to the absolute temperature. At lower temperatures conductivity increases more rapidly, supporting the theoretical expectation that the Debye relationship will not hold below Debye temperature. In every real lattice harmonic vibration occurs. At temperatures above the Debye temperature, the mean free path due to scattering by anharmonic vibrations, called the umklapp process. The thermal conductivity of a perfect crystalline material above Debye temperature should also be inversely proportional to absolute temperature. Thus the conductivity of the material determined by the umklapp process may be considered a fundamental property of the material and is called lattice conductivity. Imperfections and inhomogeneities in material also acts as scattering centres of phonons and thus further reduce their mean free path. Phase transition of material are in general accompanied by anomalies in many physical properties. In dielectric substances, anomalies are often found in the specific heat, thermal conductivity, the coefficient of thermal expansion (change of volume) and other quantities, which supply us with a useful clue to discovering and confirming a new transition, and in further investigations of it. On the other hand, the main carriers of heat are thought to be the lattice waves in dielectric substances, and so it is expected that the thermal conductivity of them would show some peculiar features when phase changes take place [3]. Crystallographically, ferroelectrics belong to the crystal classes having pyroelectricity but are characterized by the fact that their polar structures are caused by a slight distortion of nonpolar ones. It is well expected that such a distorsion of ion arrangement would affect the behaviour of the vibration of ions and hence the mutual coupling of phonons. The phase change from polar to non-polar states, or vice versa, may therefore cause some anomaly in the thermal conductivity. It was reported that the thermal conductivity of barium titanate ceramic actually shows a small anomaly around the transition at 120°C [4], where the phase change from ferroelectric to paraelectric state takes place. The transition from antiferroelectric to ferroelectric lattice also affects the thermal conductivity.

Experimental procedure

The PVA used in this study was obtained from OSAKA, Hayashi chemical industries limited, Japan. It had a molecular weight of 1700 $(CH_2-CHOH)_n$. Copper was 98.5% very fine powder, aluminium (Al) metal powder 80 mesh and iron powder 99.5% from Fluka, AG, Chem. Buchs, Germany.

The polymers was dissolved in distilled water and then heated gently, using water bath for complete dissolution. After the solution attained a suitable viscosity, the desired metallic powder was added 2.5% by weight and the mixture was cast inter a glass dish and kept in a dry atmosphere for about two weeks. Thickness available was (≈350 μm).

The apparatus used for the measurements is given in the previous work [5].

The thermal conductivity K was measured at different temperatures. This was achieved by controlling the furnace heater to maintain constant temperature at the lower surface of the sample and then the temperature gradient was measured.

The Yong's modulus of poly(vinyl-alcohol) containing metals was performed using an R.L.C. Bridge, type (TESLA BM 591). The capacitance of the sample was measured (in the range 15–120 pF at 1 kHz and 1 V) at different temperatures from room temperature up to 150°C under the applied stress ($2.16\cdot10^5$ dyne/cm^2).

Temperature dependence of thermal conductivity K

Molecular solids such as polymers, have very weak attractive forces and consequently exhibit large thermal expansion e.g. rubber and polyethylene. The ability of a material to conduct heat is given by its thermal conductivity K which is defined as the quantity of heat flow Q, per unit area A, per unit time t, per unit temperature gradient $\mathrm{d}T/\mathrm{d}X$, i.e.

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -KA\frac{\mathrm{d}T}{\mathrm{d}X}$$

where the negative sign indicates that the heat flow is in the direction of decreasing temperature.

The best thermal conductors are metals in which the free electrons are dominant and very mobile. Non metallic material conducts primarily by phonons and in general K is much smaller for these materials than for metals because of the reduced mean free path and velocity. Note the influence of density on velocity; light elements tend to have high thermal conductivities. Some non-metallic materials have a value for K in excess of that of metal, these substances which can be manufactured almost to crystalline perfection. The lack of defects assure large phonon mean free paths and hence a large K (diamond and sapphire). In contrast, in amorphous materials the random structure interferes with the movements of phonons so that K is lower than the crystalline counterpart. It has been seen that for most materials the properties of thermal conduction are determined by the electronic and crystalline state. Some solids have not perfect lattices but are porous containing voids, e.g. polystyrene. The voids represent regions of very poor thermal conduction since air is a poor conductor and so the material as a whole has a low value of K. Such materials represents a most important group of commercial thermally insulating materials.

We have now measured the thermal conductivity of poly(vinyl-alcohol) as a pure sample and PVA containing Cu, Al and Fe. As shown in Fig. 1 different additions cause a large anomaly in the thermal conductivity. The pure sample of PVA have the lowest values of thermal conductivity and the PVA+Fe have the highest values. That is because the porosity of the pure sample is greater than the other samples which are doped with metals. The heat transport through lattice vibrations (phonons) is mainly important for insulators and polymers.

For all samples the thermal conductivity K increases up to a certain temperature T_{gg}(120–160°C), which is considered a transition temperature for PVA. In this temperature range the phonon concentration increases with temperature and

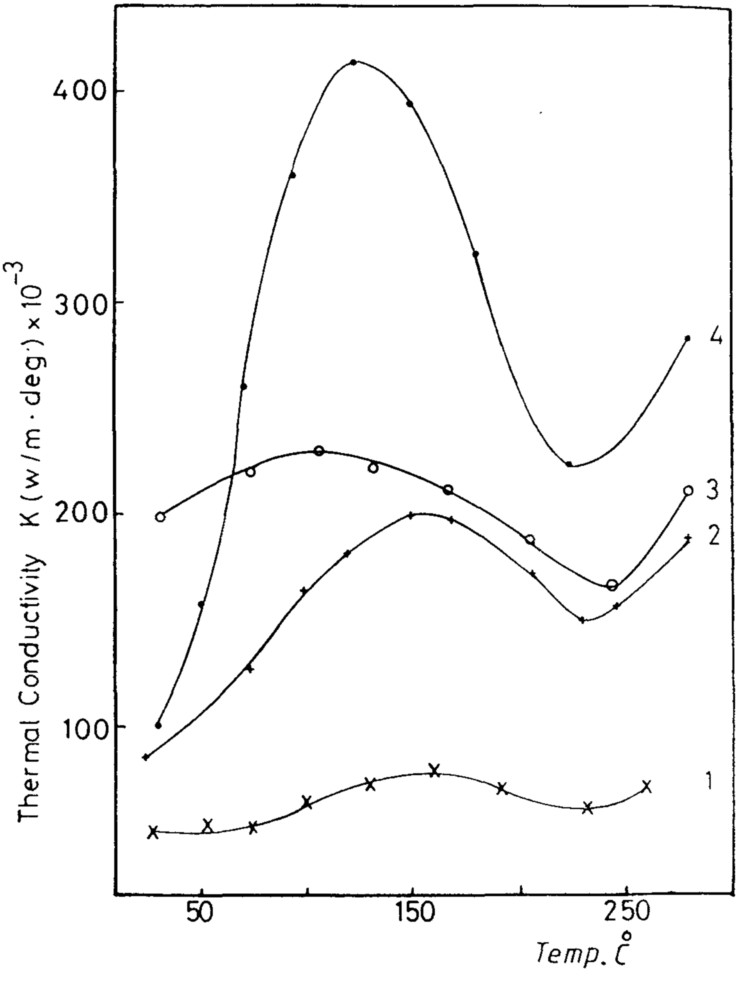

Fig. 1 Temperature dependence of thermal conductivity (K)

the inelastic scattering processes take place leading to the increase of thermal conductivity. Above T_{gg} the wagging motion of the vinyl ring will cause elastic scattering [6, 7] of phonons, causing a decrease of their mean free path and so their thermal conductivity K, which decreases up to a certain temperature T_g (glass rubbes transition) at about 220°C. Above this temperature the main chain segments of the polymers is moved, which added more lattice vibration and increase again the concentration of phonons and K.

Temperature dependence of the specific heat c

The specific heat is the change in the thermal energy of a solid in one degree change in its temperature [8]

$$c=\frac{dE_{\text{lattice}}}{dT}$$

Figure 2 shows the temperature dependence of the specific heat for pure PVA and PVA composites at the temperature range from room temperature up to 160°. The pure PVA has highest values of c and PVA containing Cu has low-

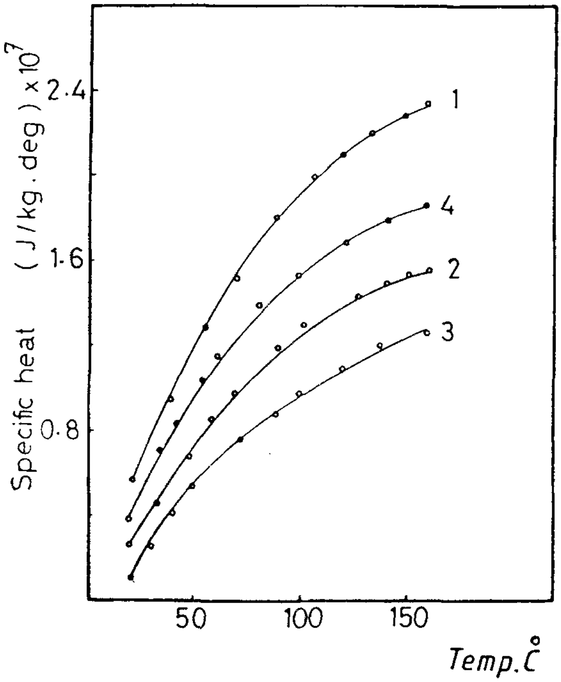

Fig. 2 Temperature dependence of specific heat (c)

est values of c. For all samples the specific heat increases with temperature up to 120°C $\approx T_{gg}$. Above T_{gg} the specific heat is nearly independent on the temperature. This behaviour may be discussed as the following:

If we consider the $T_{gg} \approx$ Debye temperature for this type of polymer, so for temperature below than Debye temperature, the energy of the material increases with temperature by means of two mechanisms:

1. The rise in probability of its excitation.
2. The increase in the number of the normal modes of lattice vibration.

The first mechanism is proportional to T and the second is proportional to T^3. Therefore E_{lattice} is proportional to T^4 and the rise in c is proportional to T^3.

In high temperature range all normal modes of the lattice are excited at the Debye temperature and a further rise in temperature cannot increase their number. Therefore the variation in energy only due to the rise in intensity of the normal modes, i.e. $E_{\text{lattice}}\ \alpha T$ and specific heat must be independent of T.

Temperature dependence of mean free path

The distance which is travelled by the phonon in the material between two collisions depends strongly on the phonon energy. It is very high for weak energy phonons and very small for high energy phonons.

The formula by Dugdale and MacDonald [9] giving the theoretical evaluation of the mean free path (L)

$$L = \frac{A_o}{3B\gamma T}$$

where A_o, B, γ mean the nearest neighbour distance, linear coefficient of thermal expansion and Gruneisen constant. γ is expressed as

$$\gamma = \frac{3\beta}{xc}$$

where x is the compressibility and c the specific heat per unit volume. On the other hand the experimental value of L is defined by the formula [3]

$$K = \frac{1}{3}cvL$$

where v is the mean group velocity of phonons.

Completely harmonic vibrations of the lattice would offer no resistance to the flow of phonons, and the mean free path as well as the thermal conductivity of such a body would be infinite. In a real body a number of scattering mechanisms which limit the mean free path of phonons may be operative. Klemans [10] has shown that if more than one mechanism is present, the over all mean free path due to the several processes may be given by

$$\frac{1}{L}=\frac{1}{L_1}+\frac{1}{L_2}+\cdots$$

where L_1, L_2 mean free path of individual processes as long as individual processes are independent of each other.

The mean free path due to scattering by anharmonic vibrations, called the umklapp process which proportional to the inverse of absolute temperature [1]:

$$L\propto\frac{1}{T}$$

Imperfections and inhomogeneities in the material also act as scattering centres of phonons, and thus further reduce their mean free path.

At low temperature the mean free path due to boundary scattering is accountable. At room temperature and above the contribution of boundary scattering to the total mean free path should be negligible, whereas the scattering of phonons at grain boundaries and pores should be negligible at room temperature and above.

The mean free path for PVA pure and PVA containing metals are plotted versus temperature as shown in Fig. 3. It is noticed that the pure sample have lowest values of mean free path and slightly dependent on temperature. The other samples of PVA+metals showed a high dependent on temperature and their mean free path is rapidly decreasing with the temperature up to about (120–140°C). Above this temperature L increases again with the temperature. The sharp decrease of L may be attributed to the increase of the probability of collision of phonons with new excited phonons due to lattice vibration. Moreover the presence of impurity increase the collision probability and more decrease the mean free path. Above the T_{gg} temperature, the vinyl ring makes a wagging motion which can be understand physically as the (rotational vibrational) rearrangement of small side groups, which reduces the imperfection and lattice defects leading to a lower resistance to the flow of phonons and the increase of the means free path. The pure PVA has small values of mean free path because the conduction process of heat dealing only by mean of phonons which have mean free paths about one tenth of those of electrons. As shown in Fig. 3, L for PVA+Al=2 Å and for pure sample ≈0.2Å at room temperature.

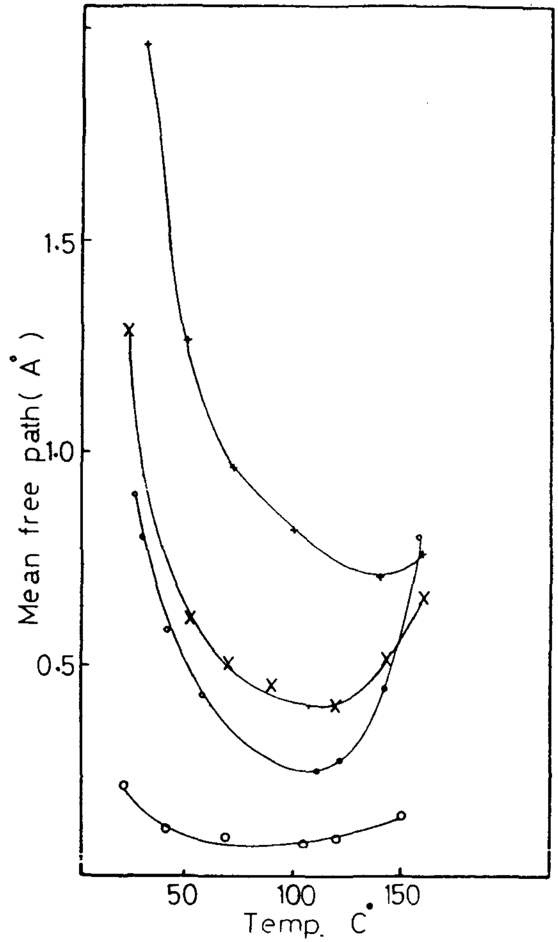

Fig. 3 Temperature dependence of mean free path (*L*)

Temperature dependence of phonon velocity

The velocity of phonons regarded as an elastic wave is determined by the elastic constants of the medium [11]:

$$v = \left(\frac{Y}{\rho}\right)^{1/2}$$

where Y is Young's modulus and ρ is the density.

The velocity of phonons for pure PVA and PVA containing metals is shown in Fig. 4 at different temperature.

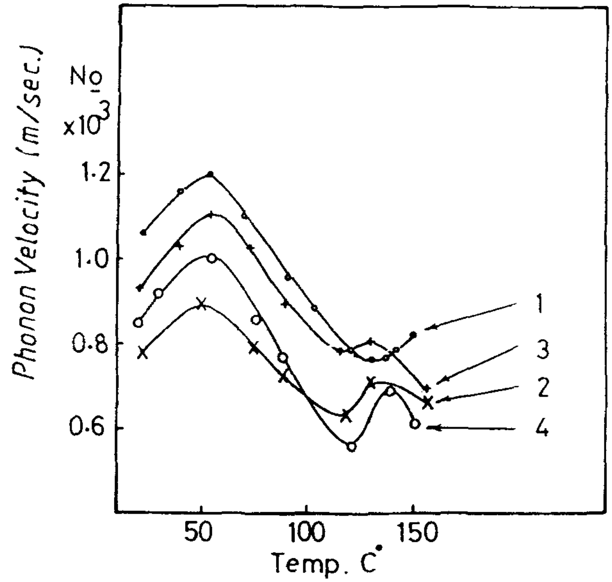

Fig. 4 Temperature dependence of phonon velocity (ν)

From room temperature up to 50°C the material is thermally excited and the lattice vibration takes place. The thermal phonons which appear from the lattice vibration are still small. Their energy E_{ph} and their velocity depend on the absorbed thermal energy by the lattice. So the velocity of phonons increases with the temperature. Above 50°C new excited phonons collide with the present phonons increasing the probability of collision; and decreasing the velocity of phonons up to 120°C which is near the T_{gg} temperature of PVA. At this temperature the phonon velocity reaches its minimum value. The wagging motion of vinyl ring decreases the imperfection and so increases the velocity to a certain limit at 130°C. Above this temperature the velocity of phonons decreases due to the motion of the main chain segments which reach at 220°C. The phonon velocity of the pure PVA has higher values than that of the PVA containing metal. The PVA pure has higher values of specific heat than the other samples as shown in Fig. 3, so the heat absorbed by lattice in pure PVA is larger than that of PVA with metals. This suggests that the phonon velocity of pure PVA must be larger than that of PVA containing metal.

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Zusammenfassung — Mit Hilfe eines Gießverfahrens wurden ≈350 μm Filme aus Polyvinylalkohol mit Gehalt an sehr feinem Metallpulver aus Kupfer (Cu), Aluminium (Al) und Eisen (Fe) hergestellt. Es wurden thermische Leitfähigkeit, Phononengeschwindigkeit, mittlere freie Weglänge und spezifische Wärme untersucht. Die thermische Leitfähigkeit von reinem PVA besitzt geringere Werte als die von PVA mit Metallzusatz. Für alle Proben steigt die thermische Leitfähigkeit K bis zu einer gewissen Temperatur T_{gg} (120–160°C) und sinkt dann mit zunehmender Temperatur wieder ab. Die spezifische Wärme steigt bis z einer Temperatur von etwa 120°C und ist darüber annähernd temperaturunabhängig. Die reinen PVA-Proben weisen bei Raumtemperatur kleine Werte für die mittlere freie Weglänge auf (L beträgt etwa 0.2 Å), jedoch für PVA + Metall beträgt L etwa 2.0 Å. Die Phenonengeschwindigkeit für reines PVA ist größer als für PVA mit Metallgehalt.