Determination of Thermal Diffusivity of Polypyrrole and Polypyrrole/Bismuth Oxide Conducting Polymers using Laser Flash Technique

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Abstract: The determination of conducting polymer's thermal properties is essential in engineering processes and design. Thermal diffusivity is one of the important thermal properties in non-steady state situations. This fundamental knowledge is useful in the development of processes and control, selection of materials and prediction of end use properties in many engineering process and design. In this research, laser flash technique is employed to determine the thermal diffusivity of Polypyrrole and Polypyrrole/Bismuth Oxide conducting polymers. Measurements were carried out from room temperature up to 420 K. It was observed that the presence of secondary doping agent of bismuth oxide enhanced the thermal properties of polypyrrole conducting polymer.

Key words: Polypyrrole, iron (3) chloride 6-hydrate, bismuth oxide, laser flash, thermal diffusivity, thermal

INTRODUCTION

Thermal diffusivity a and thermal conductivity λ can be obtained by measuring the thermal diffusivity of α, specific heat C_p and density ρ as a function of temperature. Equation 1 is as follows:

$$\alpha(T) = \frac{\lambda(T)}{C_p(T).\rho(T)} \qquad (1)$$

There are several different methods in determining the thermal diffusivity and thermal diffusivity values that can be found in the literature including hot wire and laser flash and they can be divided into two major classes which are the direct and indirect methods (Dos Santos *et al.*, 2005). Laser flash for instance, is a direct method in determining thermal diffusivity and indirect method in determining thermal conductivity. The direct method is a method in which the desired property is obtained directly from experimental results while the indirect method is where the property is derived from other properties obtained from the experiment results. In this study, thermal conductivity is derived from thermal diffusivity with an additional knowledge of specific heat and bulk density. Laser flash is also labeled as absolute and non-steady method where no standard body is required for the experiment and the property is measured, according to the transient regime of heat exchange. This method also falls under the transient heat flux method as thermal diffusivity is evaluated from recorded temperature history on rear face after being a heat pulse of incident of the front face of the sample.

Laser flash by far is the most widely used instrument for measuring thermal diffusivity. It is estimated that 80% of this measurement is conducted worldwide. This method has several advantages over a direct measurement of thermal conductivity as it is a facile method which offers rapid data acquisition, allows for a small test piece size and produces great accuracy. Meeting the requirement of a very small sample is very important as a homogenous sample may be obtained and in terms of economic and technical reasons, small size is favorable. As a non-steady method, it has the advantage of being relatively quick and less affected by errors arising from radiation loss or temperature drifts: it is, therefore, particularly suitable for measuring even poor thermal conductors and for high temperature measurement, in general (Chen *et al.*, 1977). Different types of sample perform different ranges of thermal diffusivity values. Three range of thermal diffusivity values are low diffusivity between 1×10^{-8}-1×10^{-6} m^2 sec^{-1}, medium diffusivity between 1×10^{-6}-5×10^{-5} m^{2}sec^{-1} and high diffusivity between 5×10^{-5}-1.2×10^{-3} m^2 sec^{-1}. The first range is normally dominated by polymer, followed by ceramics in the second range and metal such as copper in the last group.

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The objective of current investigation was to determine thermal diffusivity through the laser flash technique of Polypyrrole and Polypyrrole/Bismuth Oxide conducting polymers. The variation in thermal diffusivity was determined in the temperature range of 300-420 K.

MATERIALS AND METHODS

Experiments: In this research, Pyrrole (Across) was used as the monomer for the synthesis of PPy. Prior to use, pyrrole was double distilled at a temperature of 131°C at atmospheric pressure and stored at 4°C avoiding air. Iron (3) chloride hexahydrate ($FeCl_3 6H_2O$) (Hamburg) was used as primary doping agent while bismuth oxide (Aldrich) was introduced in conducting polymer polypyrrole as secondary doping agent. Iron (3) chloride hexahydrate and bismuth oxide were used without any further purification except for pyrrole. Distilled water was used in this research.

Pyyrole of 0.2 mole concentrations was mixed with 0.4-0.6 mole $FeCl_3$ as the primary doping agent together with bismuth oxide dissolved in water. The concentrations were stirred for 6 h at room temperature. Bismuth oxide was added to the polypyrrole solutions in a proper quantity of 5, 10, 15 and 20% w/w content of polypyrrole. The resulting powder was then filtered and washed thoroughly with distilled water to wash the adhered Fe^{3+} before being dried under vacuum at 50°C for 36 h. These steps were repeated for various mole ratios of oxidant/pyrrole. The sample was then ground into fine powder and pressed into pellet at 7 ton/cm^2 pressure using a Carver hydraulic presses and was polished using fine 2000 grit sandpaper to ensure the surface of each pellet is parallel, apart from removing any impurities.

The thermal diffusivity value of 2 MR and 3 MY polypyrrole and polypyrrole conducting polymer with the presence of bismuth oxide between 5 and 20% was obtained directly through laser flash apparatus model NETZSCH LFA 457 MicroFlash^{TM}-1100°C Version, ranging from room temperature up to 420 K with an interval of 20 K.

RESULTS AND DISCUSSION

The variations of thermal diffusivity of 2, 3 MR Polypyrrole and Polypyrrole/Bismuth Oxide with the presence of 5-20% of bismuth oxide have been studied from 300-420 K. The variations of these thermal transport properties with their temperatures are shown in Fig. 1 and 2 and in Table 1. The values of thermal diffusivity observed for all samples are of the expected values and fall in the same range as found in the literature
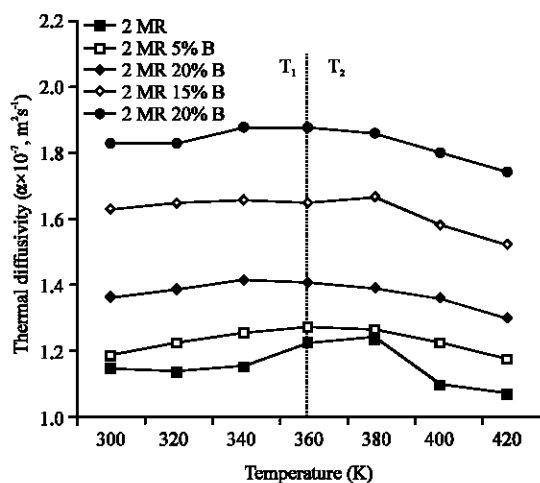

Fig. 1: Thermal diffusivity of 2 MR polypyrrole as a function of bismuth oxide concentration at different temperatures
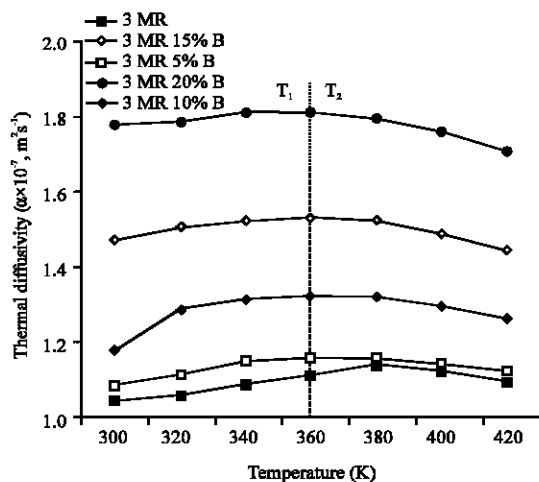

Fig. 2: Thermal diffusivity of 3 MR polypyrrole as a function of bismuth oxide concentration at different temperatures

(Da Costa and Siqueira, 1996; Joshi *et al.*, 2006; Iguchi *et al.*, 2007; Norfazlinayati, 2009; Afarin, 2012). All values in Fig. 1 and 2 show that there is a common trend concerning the thermal diffusivity dependence with temperature. For each sample, two temperature regions were observed where the first region was denoted as T_1 which shows a slight increase of thermal diffusivity with increasing temperature. Another region is marked as T_2, showing a fall-off of thermal diffusivity with increasing temperature.

It is observed that thermal diffusivity of samples of 2 MR polypyrrole and 2 MR Polypyrrole/Bismuth Oxide

Table 1: Value of thermal diffusivity for Polypyrrole and Polypyrrole/Bismuth Oxide conducting polymer

| Samples/Temperature (K) | Thermal diffusivity ($a \times 10^{-7}$, m^2sec^{-1}) | | | | | | |
	300	320	340	360	380	400	420
2 MR PPy	1.11	1.09	1.11	1.18	1.20	1.05	1.02
2 MR PPy 5% bismuth oxide	1.14	1.18	1.21	1.23	1.22	1.18	1.13
2 MR PPy 10% bismuth oxide	1.32	1.35	1.38	1.37	1.35	1.32	1.26
2 MR PPy 15% bismuth oxide	1.81	1.81	1.86	1.86	1.84	1.78	1.72
2 MR PPy 20% bismuth oxide	1.60	1.62	1.63	1.62	1.64	1.55	1.49
3 MR PPy	1.00	1.02	1.05	1.08	1.10	1.09	1.08
3 MR PPy 5% bismuth oxide	1.05	1.08	1.12	1.13	1.13	1.11	1.09
3 MR PPy 10% bismuth oxide	1.49	1.53	1.55	1.56	1.55	1.51	1.46
3 MR PPy 15% bismuth oxide	1.15	1.28	1.31	1.32	1.32	1.29	1.25
3 MR PPy 20% bismuth oxide	1.84	1.85	1.88	1.88	1.86	1.82	1.76

with the presence of 5-20% of bismuth oxide, increases to the specific maximum temperature of 380 K before a fall-off with a further increase of temperature of up to 420 K. In the case of 3 MR polypyrrole and 3 MR Polypyrrole/Bismuth Oxide, the maximum temperature is at 360 K before thermal diffusivity of all samples started to decrease with temperature. Thermal diffusivity sensitively reflects the chemical, molecular and supramolecular structure of the polymer and is believed to have an effect and due to its relation with several properties such as molecular weight, molecular orientation pressure and degree of crystallinity (Wynter, 1978). In conducting polymer, the diffusion of heat mechanism depends on the conjugation chain length in order to allow a free movement of electron. The heat energy is carried by electron which migrates along the polymer chain and then transferred from one chain to a neighbouring chain. Thus, the dopant plays an important role on the conjugation length. In this research, it is found that the primary doping agent does not affect thermal diffusivity. The increment of thermal diffusivity can be seen obviously after the introduction of secondary doping agent, bismuth oxide. It is believed that as bismuth oxide concentration is increased in polypyrrole conducting polymer, the conjugation length increases simultaneously and provides more through-space pathways for electron to migrate (Nguyen and Schwartz, 2002). At this state, the electrons wander easily along the polymer chain and move freely to another chain. Hence, the rate of energy transfer is increased (Norfazlinayati, 2009).

The transition temperature observed in this research is around 360-380 K which is common for most polymers and it is known to have syndiotactic conformation. Syndiotactic is a polymer whose monomer units are oriented alternately between dextro and levo or a polymer structure in which a monomer unit is attached to the polymer backbone in a-b-a-b fashion. In the case of phonon discussed above and will be further discussed below, it characterized the process of transformation from longitudinal to transverse phonon (Bhowmick and Pattanayak, 1990). The transition temperature observed in

the research could also be related to the change of stiffness which has something to do with the change of conformation of internal rotation of skeletal bonds (Ueberreiter and Naghizadeh, 1972a, b). Under tensile stress the conformation is transferred into other conformations by internal rotation of skeletal bonds. This rotation which requires certain amount of energy is temperature independent as mentioned above. In this case of rotation, a certain free volume must be available to permit such displacement. The total free volume of the polymer increases with increasing temperature as a result of thermal expansion (Ueberreiter and Naghizadeh, 1972a, b).

It is also believed that molecular weight has been much affected by the value of thermal diffusivity below transition temperature (Hattori, 1965). The thermal diffusivity generally shifts to higher temperature as the molecular weight in increased (Ueberreiter and Naghizadeh, 1972a, b). This has been shown through this research as value of thermal diffusivity increased as the molecular weight increased from 2-3 MR Polypyrrole/Bismuth Oxide conducting polymers.

Crystallinity is also deemed as having a considerable effect on unsteady-state heat conduction. The largest molecular weight is believed to have a higher degree of crystallinity. Although, it is difficult to derive the relationship between thermal diffusivity and degree of crystallinity quantitatively, it is generally, believed that it has a strong relationship through the research reported in literature (Hattori, 1965). A system of higher thermal diffusivity values is also believed to have a stronger interaction of chain molecules compared to a system with a lower thermal diffusivity which is more rigid.

As the temperature rises in the temperature region T_2, which is beyond transition temperature, the polymer changes to rubbery through leathery state and gradually, individual units, atomic groups and small chain segments undergo intensive thermal motion and large torsional rotations and sliding of chain segments starts to play a dominant role in governing variation properties with temperature. The decrease of thermal diffusivity in the

above transition temperature indicates a change in stiffness of the polymer. The mechanism of heat diffusion depends on the medium state of the polymer itself (Norfazlinayati, 2009). As an addition, thermal diffusivity has been related to Debye Eq. 2 of:

$$\lambda = \frac{1}{3}C \upsilon l \qquad (2)$$

Where:
λ = Thermal conductivity
C = The specific heat capacity per unit volume
υ = The average phonon velocity
l = The phonon mean free path

In Eq. 1, specific heat capacity at constant temperature, C_p and density, ρ is considered related to C in Eq. 2. Thus, thermal diffusivity is expected to be influenced by υ. It is believed that in the above transition temperature, the distance of polymer becomes large but is considered to decrease the velocity of phonon (υ) which results in a decrease of thermal diffusivity (Agari *et al.*, 1997).

It is interesting to note that the enhancement of thermal diffusivity comes from the introduction of 20% of bismuth oxide in 2 and 3 MR polypyrrole conducting polymer. The highest thermal diffusivity was obtained from the highest system with higher molecular weight. Larger interaction between chains molecules is believed to produce higher thermal diffusivity values (Hattori, 1965). According to the findings of this research, it is much agreeable that molecular weight has an influence over the thermal properties of polymer.

CONCLUSION

It can be concluded that the laser flash technique used in this research is an efficient technique in determining the thermal diffusivity in conducting polymer materials. The thermal diffusivity values observed in this research for Polypyrrole and Polypyrrole/Bismuth Oxide conducting polymers range from $1.02\text{-}1.88 \times 10^{-7}\,\text{m}^2\text{sec}^{-1}$ and is applicable as they lie in the range of conducting polymer reported in literature. It is observed that the impregnations of bismuth oxide in conducting polymer polypyrrole has boosted the thermal properties of the system. This could be due to higher molecular weight, larger interaction between chain molecules and higher crystallinity which have influenced the thermal properties of materials.

SUGGESTIONS

It is suggested that the increment of thermal diffusivity can be due to the interaction between the framework of bismuth oxide and polypyrrole, thus, increases phonon velocity. The phonon transport can be assumed to occur preferably, through, these materials due to higher number of phonon vibrational modes and the higher length of path in bismuth oxide compared to polypyrrole (Afarin, 2012). As mentioned earlier, crystallinity is believed to have an impact on the value of thermal diffusivity. Higher crystallinity shows a larger value of thermal diffusivity compared to lower crystallinity material (Wynter, 1978). As bismuth oxide is introduced in the polypyrrole system, a great percentage of crystallinity has also been increased. This indicates a great effect in which the percent crystallinity has on thermal diffusivity of Polypyrrole/Bismuth Oxide conducting polymer.

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