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THE ANNEALING EFFECT ON THERMAL DIFFUSIVITY OF POLYANILINE (EMERALDINE BASE) MEASURED USING PHOTOFLASH TECHNIQUE

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ABSTRACT

In this paper, we present the annealing effect on thermal diffusivity of Emeraldine Base–Polyaniline (EB). The thermal diffusivity was measured at room temperature using photoflash technique. The excitation source used consists of a high intensity camera flash. A series of samples annealed at different temperature (25 °C, 100 °C, 150 °C, 200 °C, 250 °C and 300 °C) were investigated and the annealing effect on the thermal diffusivity was discussed in detail. The Scanning Electron Microscopy (SEM) and X–ray Diffraction (XRD) measurement was done to analyze the annealing effect on morphology and sample structure.

INTRODUCTION

Polyaniline has emerged as a potential conductive material due to its comparatively good environmental stability, easy preparation and wide areas for its applications such as rechargeable batteries, electromagnetic interference shielding, light emitting diodes, display devices, biosensors [1]. From the industrial point of view, the fabrication of a thermally processable polyaniline would be preferable because it is easier and much cheaper. This material would be useful due to its ability to be thermally processed into useful product using conventional techniques such as extrusion, stretching, rolling and etc., which generally carried out at elevated temperature [2].

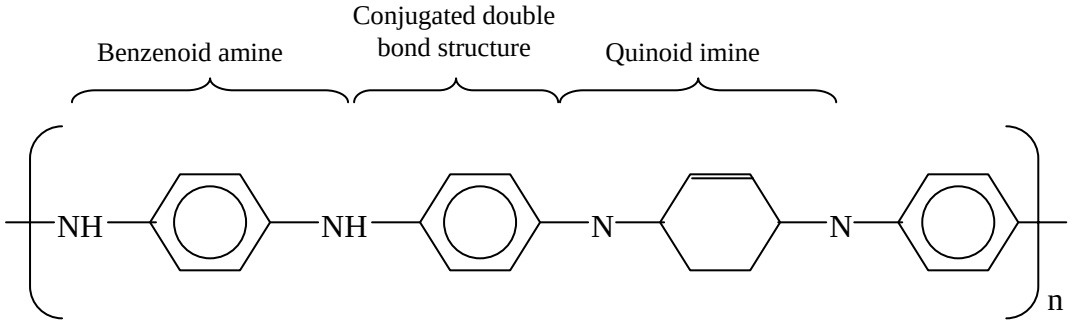


Figure 1: Structural formula of Polyaniline (Emeraldine Base)

Polyaniline is a polymer which results from oxidative polymerization of aniline to yield (B–NH–B–NH) or (B–N=Q=N–) where B denotes benzenoid and Q denotes quinoid structure. Thus based on the ratio of amine to imine gives the four forms, namely emeraldine base (neutral), leucoemeraldine (reduced), emeraldine salt (conducting) and pernigraniline (oxidized). It has a conjugated double bond structure (the benzenoid ring) between the quinoid imine and the benzenoid amine structures, which renders the polymer a candidate as an electrically conductive polymer (Figure 1).

Flash method, originally described by Parker et. al. [3] is a transient heat flow technique primarily used to measure the thermal diffusivity of the materials. Thermal diffusivity is a measure of how quickly a temperature disturbance can propagate through a material and is related to the thermal conductivity through the following equation

$$\alpha = \frac{\lambda}{\rho C_p} \quad (1)$$

This relationship allows the thermal conductivity (λ) to be calculated if thermal diffusivity (α), bulk density (ρ) and specific heat (C_p) are known. The photoflash method involves rapidly heating one face of a small disk or slab of the material with a single pulse and monitoring the arrival of the resulting temperature disturbance as a function of time on the other face of the sample. The thermal diffusivity is calculated from the characteristic curve (thermogram) of the temperature excursion of its rear surface [3] as

$$\alpha = \frac{1.37L^2}{\pi^2 t_{1/2}} \quad (2)$$

where L is the thickness of the sample and $t_{1/2}$ is the time required for the back surface of the specimen to reach half the maximum temperature rise.

In this paper, a study of the thermal diffusivity of EB was performed to examine the annealing effect on the thermal diffusivity value and identify the optimum processing and maximum application temperatures. Characterization of the EB samples in different annealing temperature have also been carried out using X–Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The comprehensive studies of heat-treated EB allow us to understand the thermal diffusivity and thermal stability of this unique polymer.

EXPERIMENTAL SETUP

The photoflash detection system consists of a light source (A), sample holder (B), thermocouple (C), low noise preamplifier (D), oscilloscope (E), photodiode (F) and personal computer (G) as shown in Figure 2. A normal electronic camera flash (Maxxum, model 5400HS) was located 2 cm in front of the sample as an energy pulse source. A disk–shaped sample is placed on the sample holder attached to the thermocouple. The front block of the sample was covered with the aluminium foil to shield the light from the photoflash. The top cover of the holder has a hole smaller than the sample's diameter to ensure that little front face is obscured.

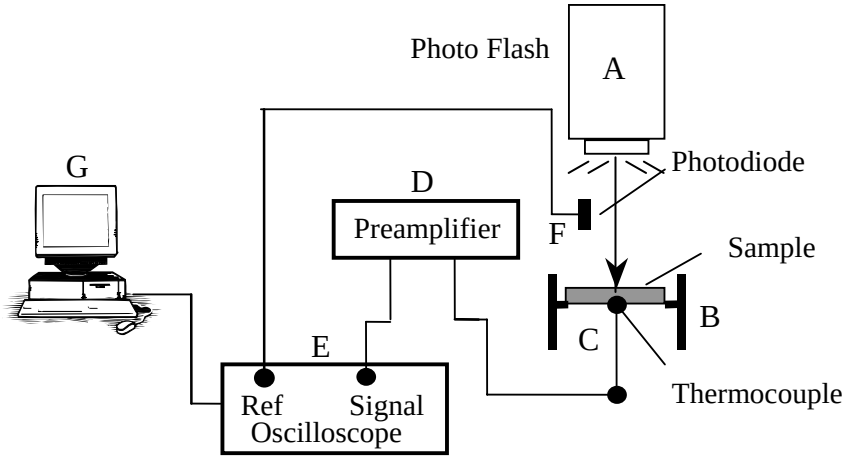


Figure 2: Schematic experiment setup of the photoflash technique

In this setup, a fast response K–type thermocouple was attached directly to the rear surface of the sample to monitor the temperature at the rear surface of the sample. The signal from the thermocouple was then amplified by a preamplifier (SR560) and monitored with the digital oscilloscope (Tektronix TDS 220). The signal was then analyzed for the thermal diffusivity value using equation (2). The photodiode (model RS 308–067) was used to trigger the oscilloscope. 10 minutes was allowed between the measurements in order to make sure the sample reach the initial temperature (room temperature). The measurements were repeated three times for each sample.

SAMPLES PREPARATION

EB in powder forms were supplied by Zipperling Kessler & Co (Germany) with quoted particle size ranges from 3 to 100 μm. This powder was used as received without any further purification or drying. EB powders were placed into the 8 mm diameter mould to form a pellet shape sample using a 12 HP pressing machine (ShiChyan Electric & Industrial Co. Ltd). The compression pressure applied onto the mould was 250 psi. Then, the sample was placed in the alumina boats and was heated in air using an oven (Nabertherm, Germany). The process of annealing was carried out at a temperature raised from room temperature, $25\,^{o}C$ to $100\,^{o}C$, $150\,^{o}C$, $200\,^{o}C$, $250\,^{o}C$ and $300\,^{o}C$. The heating rate was $5\,^{o}C$ /minute. The maximum temperature was maintained for 30 minutes. The samples were allowed to cool naturally to room temperature for 24 hours.

RESULTS AND DISCUSSION

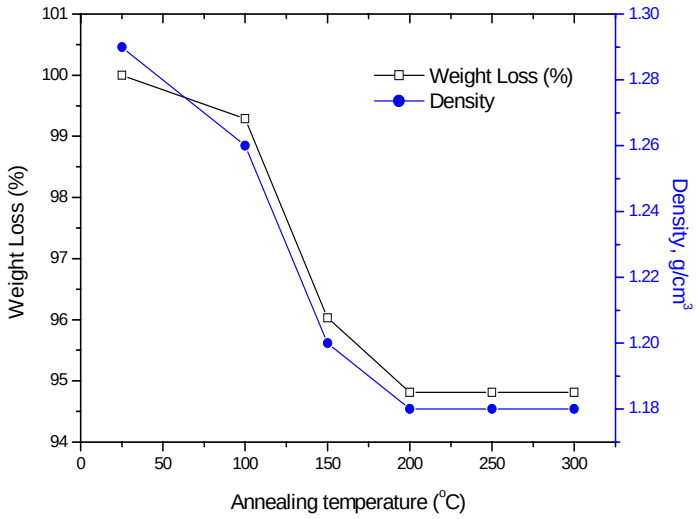


Figure 3: Relation between weight loss (%) and density of the EB sample prepared at different annealing temperature

Figure 3 shows the weight loss percentage and density of the EB annealed at different temperatures. The sample density shows the same trend with the weight loss percentage. The 0.71% weight loss observed at 100 °C is attributed to the loss of the present water molecules initially present in the sample and to a low–molecular weight oligomers. A further weight loss up to 5.19% at 200 °C mainly attributed to the loss of the residual solvent trapped inside the amorphous phase or loss of the solvent bound to the polyaniline chain. Jousseaume et. al. [4] have interpreted this behaviour by assuming an increase of the amorphous zone volume in the materials that allows an easier displacement of chains, favoring the solvent evaporation. In the temperature range 200–300 °C, no weight loss was observed. This behaviour was attributed to the reorientation of the polyaniline chains (recrystallization) and cross-linking reaction. The decomposition did not occur since there is no weight loss in this temperature range. Based on the fact that during the annealing process weight loss was low (~5%) we could conclude that the EB has a good thermal stability particularly at this temperature range.

From figure 4, plot a represents the signal obtained from EB sample without heat treatment and the plot b represent the signal obtained from EB sample annealed at 200 °C. From the curve, we could easily determine the $t_{0.5}$ for each of the samples. It was noticed that the response time for EB annealed at 200 °C is faster than for EB without heat treatment. It is known that the faster the propagation of heat into the medium, the higher the thermal diffusivity value. Due to the fact that there is a heat loss occur, thermal diffusivity was corrected using Clark and Taylor rise–curve technique [5]. The characteristic rise time and the corrected value of thermal diffusivity of EB annealed

at different temperature are tabulated in Table 1. From the table, it is found that the finite pulse time effect is negligible because $\tau / t_c << 1$ [6].

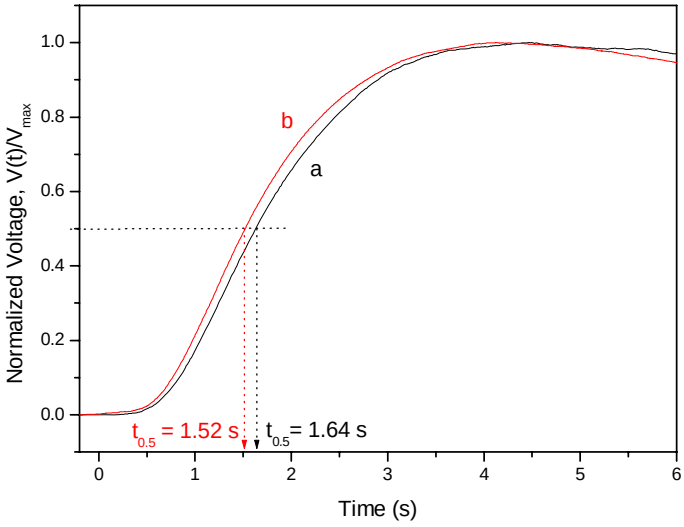


Figure 4: Thermogram for the EB sample without heat treatment (a), thermogram for the EB annealed at 200 ℃ (b).

Table 1: Characteristic rise time and the corrected value of thermal diffusivity for EB prepared at different annealing temperature

Annealing temperature on EB samples (℃)	Density (g/cm^3)	Thickness L(cm)	Characteristic rise time $t_c = L^2/\alpha\pi^2$ (s)	τ / t_c	Corrected thermal diffusivity $\alpha_{corrected} \times 10^{-3}$ (cm^2/s)
25	1.29	0.151	1.52	0.003	1.52 ± 0.03
100	1.26	0.154	1.45	0.003	1.66 ± 0.03
150	1.20	0.156	1.39	0.004	1.78 ± 0.03
200	1.18	0.157	1.33	0.004	1.88 ± 0.04
250	1.18	0.157	1.27	0.004	1.96 ± 0.04
300	1.18	0.157	1.22	0.004	2.04 ± 0.04

Figure 5 shows the thermal diffusivity of the EB as a function of annealing temperature. The thermal diffusivity value increases linearly as the annealing temperature increases. The annealing process was important to remove residual voids, improve the contact between the neighboring particles and orientate the molecules in a proper arrangement [7]. Annealing process is known to modify thermal and mechanical behaviour of polymer, this subsequently cause the changes of the thermal diffusivity value on further

annealed the sample on higher temperature [8]. It is also known that the thermal diffusivity increases as the density of the sample decreases.

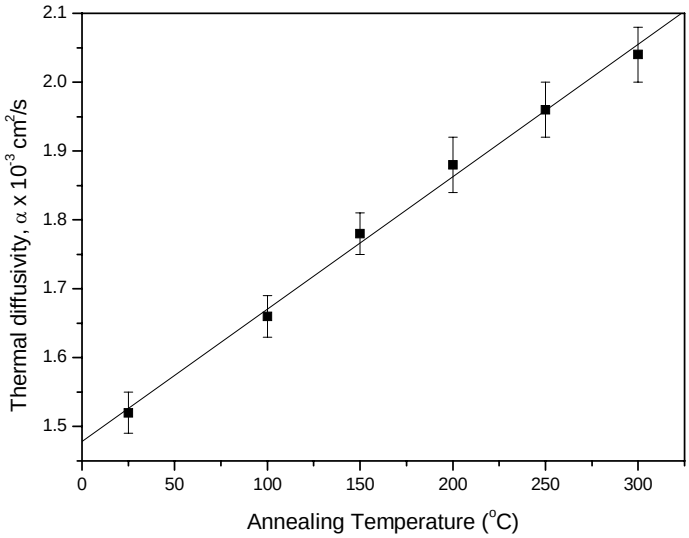


Figure 5: Thermal diffusivity of EB annealed at different temperature

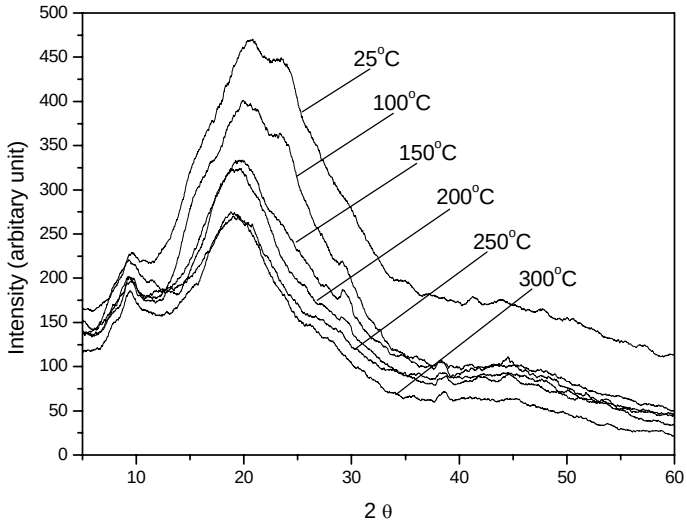
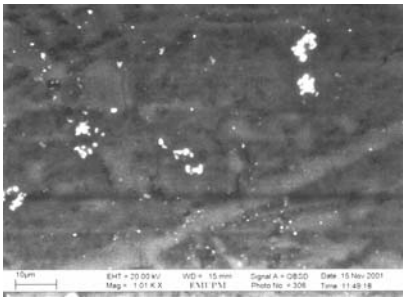


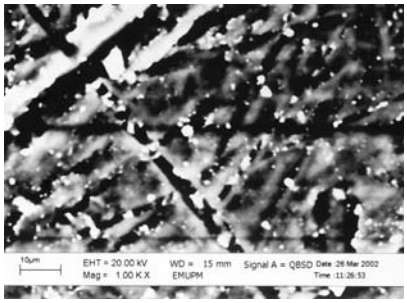
Figure 6: XRD pattern for EB annealed at different temperature

The annealed EB sample are also characterized using a computer–controlled x–ray diffractometer, XRD (Philips model 7602 EA Almelo) using Cu Kα (λ = 1.5418 Å) radiation. The diffraction patterns of these samples were obtained by scanning the samples with an interval of scanning angle (2θ) from 5^{o} to 60^{o} with a scanning speed

of 2^{o} min^{-1}. The XRD spectra are shown in Figure 6. When a polymer is annealed, its structural behaviour is altered due to the accumulation of several structural processes such as: disorientation, recrystallization by nucleation, recrystallization by growth, shrinkage, and crystal decomposition. These processes canbe induced by the annealing process [9]. The XRD spectrum shows that the degree of crystallinity of EB slightly decreases as the annealing temperature increases. Annealing process might disturb the crystalline region and increases the chain mobility, therefore increases the thermal diffusivity of the sample.



(a)



(b)

Figure 7 (a): Microstructure of EB without heat treatment
(b): Microstructure of EB annealed at 200 °C

The surface morphology of the untreated EB and EB annealed at 200 °C was investigated using scanning electron microscope, SEM (LEO model 1455 VPSEM). The morphologies of the sample surface at magnification of 1,000X are shown in Figure 7(a) and (b). It is indicated that the morphology of the untreated EB is somehow different with the EB annealed at 200 °C. The untreated sample shows smoother morphological structure than the sample annealed at 200 °C, it seems to be flourishing in the surface. The latter shows larger particles, rather than the original fine structure due to the annealing process on the EB. The EB annealed at 200 °C exhibits a coarse morphological structure after undergo the annealing process, which destroys the original aggregates of the EB.

CONCLUSION

The thermal diffusivity values of EB annealed at different temperature (25 °C, 100 °C, 150 °C, 200 °C, 250 °C and 300 °C) were investigated using a simple and inexpensive photoflash method. The thermal diffusivity value of samples EB was determined to be 1.52×10^{-3} cm^2/s to $2.04\times10^{-2}\times10^{-3}$ cm^2/s corresponds to the samples annealed from 25 °C to 300 °C. It was found that the thermal diffusivity value of the EB samples increased as the annealing temperature of the EB increased. It was also observed that the result from the XRD and SEM are supporting the thermal diffusivity behaviour revealed in the present measurements.

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