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Thermal Properties of Chemically Prepared Emeraldine-Base Form Polyaniline

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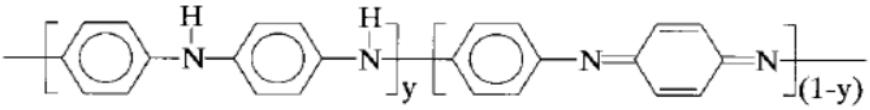
ABSTRACT

In this work, pure emeraldine base (EB)-form of Polyaniline (PANI) powder was chemically prepared in 1M HCl aqueous solution. The thermal characteristics and chemical structures of this powder were studied by differential scanning calorimetric (DSC), thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). A polarizing optical microscope was also used to examine the morphology of this sample. The results show that the EB-PANI powder had observablemoisture content. Moreover, in the first run of DSC thermal analysis, the exothermic peak about 170–345°C was due to the interlocking reaction occurring among the EB-PANI molecular chains. X-rayand FTIR examinations further confirmed the chemical interlocking reaction during thermal treatment. TGA results provided that there were two major stages of weight loss for EB-PANI sample. The first weight loss, at the lowest temperature, resulted from an evaporation of moisture. Theother weight loss, at the highest temperature, was due to the chemical structure degradation of the sample. Degradation temperature of the pure PANI powder was around 450°C. The degradation temperature of emeraldine salt ES-PANI was lower than 360– 400°C, than that of the EB-form. From TGA results, weapproximately estimated that 2.7 Aniline of repeat units, on average, were doped with 1MHCl molecule in the ES-PANI. Single crystal morphology found of EB-PANI, mostly like a conifer leaf.

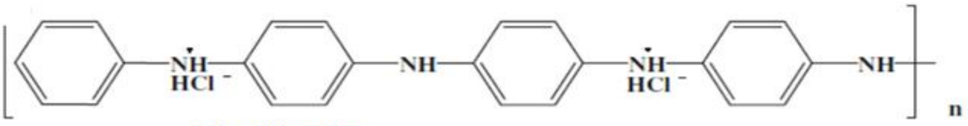
Keywords-*Thermal characteristics, EB-PANI, XRD, DSC, morphology*

I. INTRODUCTION

Polyaniline (PANI) is one of very important member in the family of conducting polymers materials (CPs). MacDiarmid [1], a first one an exemplifiedthat the chemical structure of Polyaniline could be diagramed by the following formula:



Where the value (1 – y) topresents the chemical oxidation of PANI. The value of y can be varied from y ~ 1 (leucoemeraldine base LB) to y ~ 0 (pernigraniline base PB). If y~ 0.5, the PANI is referred to as (emeraldine base EB). This form of EB-PANI cannot be dissolved in the common organic solvents. However, it can be dissolved an inorganic solvents as Chloroform and NMP. Then, pure form of PANI films can be cast from the NMP solution [2,3].Furthermore, EB-PANI can be doped in a protonic acid, such as HCl or H_2SO_4, and transferred to emeraldine salt form as (ES-PANI),with a moderately high level conductivity up to 10–100 S.cm^{-1}.Generally, chemical oxidization method synthesis is the major way for the fabrication of PANI [4,5].Chemical oxidation polymerization process is particularly important because this synthesis is the most feasible method for makingPANI powder on a micro-scale. Due to PANI has an good environmental stability and unusually electrochemicalcharacteristics, many of scientific applications of PANI have been studied and developed, such as rechargeablebatteries [6,7] biosensors [8,9] protections of corrosion [10,11]and antistatic materials [12].However, due toit's a poor thermal processing properties the commercial applications of PANI have been limited. Therehave been several reports focusing on the thermal and mechanicalcharacter of PolyanilinePANI. Wei [3, 4],investigated the thermal transitions and mechanical properties of films of chemical fabricated PANI. They also studied the thermal characteristics of chemical oxidativesynthesized PANI with variantdopants [13].Chen [5]discussed the thermal analysis, chemical structure,and doping behavior of prepared PANIplasticized with HCl solvent. Stevenson [14] investigatedthe thermal degradation of HCl-doped EB-PANI.Gregory [15]studied thermal properties of chemical prepared PANI. Chandrakanthiand Careem [16]presented study on thermal properties to examine the thermal stability of polymers material andto identify the optimum processing.In the previously studies, the polymerizationmethod by strong of salt ionic media were almost 1MHCl Hydrochloride acid aqueous solution. Therefore, in this study, weused 1M HCl aqueous solution as the acidic polymerizationmedia to prepare EB-PANI.A chemical structure of the ES-PANI (doped by salt ionic) can be schematically represented by the followingformula:



Polyaniline (ES)

The charged Cl- group of HCl associates with thepositively charged backbone of polymer chain.ES-PANI is not soluble in common organic solvents. In this work, we also an estimatedhow many repeating units of aniline, in average, doped with 1MHCl in doped form of PANIthe results of thermo-gravimetric analysis (TGA).The thermal properties of the PANI were studied with differential scanning calorimetric (DSC).Then studied the crystallinity andchemical microstructure of thermally undoped and undopedPANI with x-ray diffraction (XRD) and Fouriertransform infrared spectroscopy (FTIR), respectively. Through these studies, the thermal stability of EB-PANI could be estimated in moredetail. Moreover, to our knowledge, study morphology of EB-PANI crystalline from solutionwas not to show. Therefore, in this study, we fabricated 0.1wt % EB-PANI in HCl acidand observed the crystalline structure of EB-PANI. Threenecked flat-bottomed reactor was used to fabricatethe PANI polymer. A stirrer was put in the reactor toensure proper mixing. After that, solution A wasplaced into an icebath, which contained salt and was equipped with athermometer. After that temperature of solution A wascooled to 0°C, solution B was then slowly added dropby drop into solution A over a period of 3h. The oxidation process of aniline is highly an exothermic;the addition rate of solution B was properly controlled to prevent any sharp temperature increase because ofthe polymerization reaction. After 24 h, the precipitated dark green ES-form of Polyaniline was recovered fromthe reaction mixture. Furthermore, the precipitate was filtered and washed again with methanol until the methanol filtratewas colorless to remove any other byproducts. Then, the prepared ES-PANI wasconverted to EB-form PANI by stirring with of1M NH_4OH Hydroxide Ammonium solution at room temperature to overnight. At the end of the stirring, the material was filtered and dried under anoven vacuum for 48 h.Finally, 6.41 g of the dark blue EB-PANI powder.

II. MATERIALSAND REQUIRMENTS

We have used the following chemical materials for synthesis Polyaniline. All chemicals materials used here were the highest purity available, which their supplier companies and the purpose for used were listed in Table (1).

Table1: Chemicals materials andtheirsuppliercompanies.

No.	Chemical Materials	Molecular weight (g/Mole)	The Origin Company
1-	Aniline hydrochloric ($C_6H_5NH_2.HCl$)	93.13	Merck Schuchardt, Germany
2-	Ammonium persulphate $(NH_4)_2S_2O_8$	228.20	Merck KGaA, Germany
3-	Hydrochloride Acid (HCl)	36.46	BRIGHTCHEM, Penang, Malaysia

III. EXPERIMENTAL PROCEDURES

In this work, EB-PANI was prepared bychemical oxidative method with ammonium persulphateas oxidative agent on theProcedure described [2, 5]. Two solutions were prepared previously.Solution 1 was of 1M HCl aqueous solutioncontaining 0.46M of aniline. Solution 2 was 1M HCl aqueous solution containing 20g ofammonium persulphate (0.44M). A 1000ml of four-necked flat-bottomed reactor was used to preparethe PANI. A stirrer was put in the reactor toensure proper mixing. Then, the reactor was keptunder vigorously stirring. After that, solution A waspoured into this reactor, which was placed into an ice-bath, which contained salt and was equipped with athermometer. After the temperature of solution A wascooled to 0°C, solution 2 was then slowly added dropby drop into solution 1 over a period of 3 h.Because the oxidation of aniline is highly exothermic, the addition rate of solution 2 was properly controlledto prevent any sharp temperature increase because ofthe polymerization reaction. After 24 h, the precipitateddark green ES-PANI was recovered from the reaction mixture. Then, this material was filteredand washed with 400 mL of 0.1M HCl solutionfollowed by 400 mL of distilled water until the filtratewas colorless.Furthermore, the precipitate was washed again with methanol until the methanol filtratewas colorless to remove oligomers and other byproducts. Then, the prepared ES-PANI wasconverted to EB-PANI by stirring with 400 mL of1M NH_4OH solution at room temperaturefor another24 h. At the end of the stirring, the material wasfiltered and dried under a vacuum oven for 48 h.Finally, 6.48 g of the dark blue EB-PANI powder was obtained.

IV. INSTRUMENTS AND MEASUREMENTS

To study morphological examination of EB-PANI powder (0.01 g) was dissolved in 10ml of Chloroform to form a dark blue solution. For polarizingoptical examination, a drop of Chloroform solution containing the EB-PANI was placed onto a slide.Then, this slide was dried under anoven vacuum at 60°C for 48 h. Amorphological study of the thin films of PANI was carried out using field effect scanning electron microscopy (FESEM) (Model: FEI Nova Nano SEM 450) operating at 20 kV, was used toexamine the crystalline morphology of the EB-PANI.X-raydiffraction study (Model: PANalytical X pert Pro MRD PW3040) was used to analyze different EB-PANI powder samples. Thin films samples were annealedat 350, and 450°C for 1 h, respectively, andwere then leftat room temperature. XRD results were obtained in a range from 10-70° (2θ position). XRD patterns were recorded with a step width of 0.02o and step time 1.25 sec by using (CuKα) radiation (λ=1.5406Ao). The patterns were analyzed by matching the observed peaks with the standard pattern provided by JCPDS file data reference.Thermal analysis studies by DSC. A differential scanning calorimeter (Shimadzu model DSC-60, USA) was used to study the thermal characters of the EB-PANI powder in a temperaturerange from room temperature 25-350°C a heating rate of 30°C/min. After the first run finished,the sample pan containing the EB-PANI powderwas cooled to room temperature naturally 25°C. Thermogramsfor these two conditions were recorded, analyzed,and compared.FTIR analysis examination for the chemical structure of EB-PANI powder was identified byFTIR (Model: Perkin Elmer Spectrum Gx, USA) in the wavenumber range 400–4000 cm-1 with the number of scans equal to 10. Also, to examine the influence of thermaltreatment on the chemical structure of the EB-PANI, the sample analyzed by DSC was also examined by FTIR. I prepared all of the EB-PANIsamples for FTIR analysis by grinding powderysamples with KBr powder (weight ratio 1:99) andthen pressing the mixture into tablets.TGA (PerkinElmer model TGA 7, USA) was used to measure the weight loss of the EB-PANI powder in a temperature range from room temperature 25oC to 700°C at a heating rate of 30°C/min undera nitrogen stream. The weight loss of ES-PANI (HCl- doped) PANI powder in a temperature range fromroom temperature to 700°C at a heating rate of 30°C/min under a nitrogen stream was also examined.

V. RESULTS AND DISCUSSION

A. Morphological Examination:

Studies the morphological of chemically synthesized Polyaniline are important for investigating the intrinsic characteristics of the polymer [17]. Many of the studies [18-21] are rudimentary and exploratory in nature. The dependence of morphology upon variables such as different anions employed in the synthesis and difference in chemical procedures need to be investigated in detail.Fig 1 (a, b) shows the morphology of Polyaniline pure Emeraldine base (EB) form of powder polymer which synthesized at 0^o C. FESEM photo samples taken at deep magnifications at 5µm and 10µm.

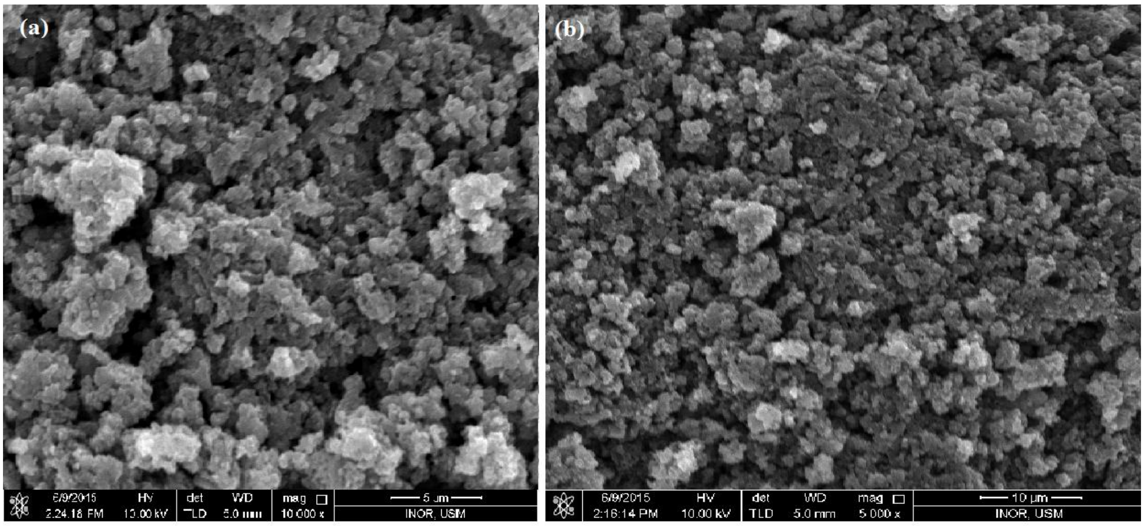


Figure1. FESEMmicrographs ofPANI-EB powdersynthesized at Magnification (a) 5μm (b) 10μm.

FESEMshow typical features of the polymer material. All photographs are mainly composed ofirregularly arranged granular. Moreover, thestructure behavior more porosity. FESEM aside from pictures shown in Fig. 1, illustrate the morphology of Polyaniline (EB) synthesized at 0^{o} C.It can be seen that the Polyaniline particles have highly micro porous type morphology and is able to increase the liquid–solid interfacial area. The highly porosity nature of the polymer material and the clumped spherical morphology was confirmed with a FESEM study [22, 23].

B. XRD Analysis:

XRD patterns studies were done by using high resolution x-ray diffraction (PAN Analytical X-PERKY Pro MRD PW3040). XRD patterns were recorded in the range 2θ from 10^{o}–70^{o} with step width 0.02^{o} using CuKα1 radiation at λ=1.5406A^{o}. The observed diffraction peaks agreed well with the standard card of polymer with orthorhombic structure. Fig 2, representing the x-ray diffraction of immaculate Polyaniline (pure) PANI-EB demonstrates a peak at 22.73^{o}; this means the PANI is an amorphous nature material, these outcomes are in agreement with previous studies [24- 26].

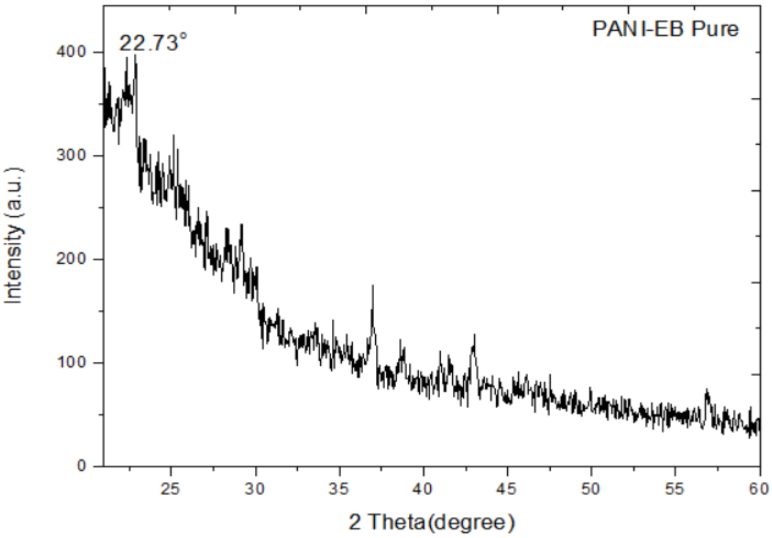


Figure2.XRD patternof PolyanilineEB.

For polymer structure as an orthorhombic crystal can be estimated from the XRD information of all planes at 2θ values taking into account d-dispersing values. For the specimens, the constants have been resolved and are recorded in Table 2. The interplanar crystallinity distance d and crystal size were calculated by Bragg's and Scherer Debye equations:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where β is the full width half maximum (FWHM). The crystalline size D of the polymer is assessed with the full width half maximum FWHM intensity of the x-beam diffraction peaks at 2θ values utilizing Debye Scherer formula.

Table2:X-ray diffractionparametersof PolyanilineSamples.

Polymer	**2θ (Degree)**	**FWHM β(°)**	**(*hkl*)**	***d* (A°)**	***D* (nm)**
PANI-EB	22.75	0.45	(021)	3.9	18.8

X-ray diffraction of PANI-EB and doped prepared at 0°C showed the partial crystalline state increased as the molecular weight grew. The increase was more obvious for the samples prepared at low temperature. This may indicate that chains under lower temperature conditions have less structural defects.

C. DSC Thermal Analysis:

DSC thermal analysis we have two curves are shown in Fig3. Fig 3(a) is the DSC thermogram of the EB-PANI in the first run. There were two peaks in Fig 3(a), an endothermic peak at 50°–160°C and an exothermic peak at 180–340°C. Therefore, the endothermic peak was most likely due to the vaporization of water. This was in agreement with the TGA results. The chemical process related to the exothermic peak was due to a crosslinking reaction. This crosslinking reaction resulted from a coupling of two neighboring -N=Q=N- groups (where Q represents the quinoid ring) to give two -NH-B-NH- groups (where B represents the benzenoid ring) through a link of the N with its neighboring quinoid ring, as suggested by Scherer et al [27]. Fig 3(b) shows the DSC thermogram of the EB-form PANI powder in the secondrun. There were almost no significant endothermic or exothermic peaks, as shown in Fig 3(b), because no apparent moisture existed in the sample. Moreover, a crosslinking reaction occurred during the firstrun DSC thermal treatment and resulted in a three dimensional chemical structure of EB-PANI. Therefore, no apparent exothermic peak was observed.

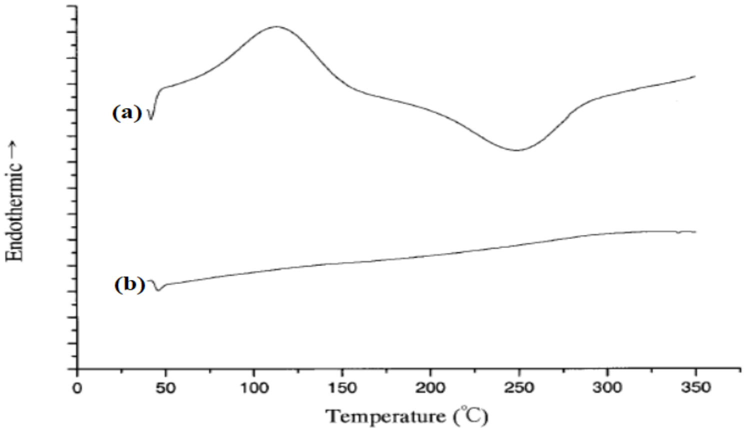


Figure 3.DSC thermal analysis curves of EB-PANI powder under N_2gas: (a) first run, and(b) second run (Heating rate ~ 20°C/min).

D. FTIR Analysis:

To investigate whether the crosslinking reaction really occurred, the FTIR examination was conducted at room temperature. Two of EB-PANI samples were examined untreated and treated by DSC thermal analysis. The results are illustrated in Fig 4. Fig 4(A) shows the FTIR results of the EB-PANI without DSC thermal analysis. Fig 4(B) shows the FTIR results of the EB-PANI powder treated by DSC thermal analysis (first run). The intensity ratios of the FTIR absorption of the C=C stretching vibration of quinoid rings (1592 cm^{-1}) to that of benzenoid rings (1508 cm^{-1}) and the electronic like absorption peak of -N=Q=N- (1150 cm^{-1}) both decreased when the EB-PANI powder was treated by DSC thermal analysis. These results proved the occurrence of the crosslinking reaction from quinoid rings to benzenoid rings. Figure 3 illustrates the thermal crosslinking reaction among EB-form PANI, molecular chains [27].

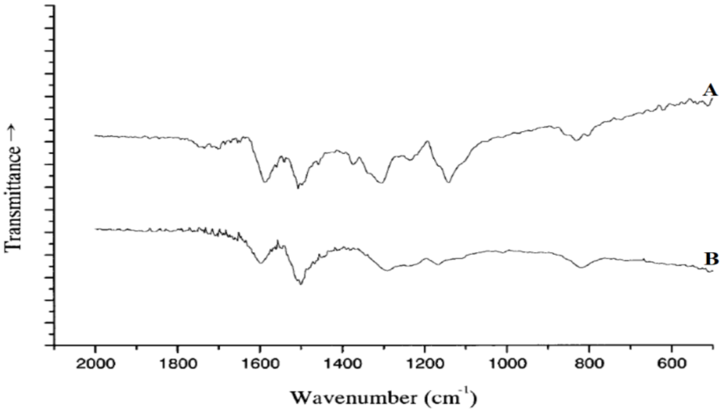


Figure 4;FTIR of EB-pure PANI: (A) unanalyzed and (B) analyzed by DSC at first run.

E. TGA Analysis:

Fig.5, shows that the moisture and HCl contentsof ES-form PANI were around 10% (ΔY1) and 18%(ΔY2), respectively. Therefore, the weight percentageof PANI should have been around 70%. To findhow many monomer aniline repeating units doped with 1 molecule in PANI, we set up eq. (1):

$$\frac{100-\Delta Y1-\Delta Y2}{\Delta Y2}=\frac{M1*X}{M2*1}................(1)$$

Where (ΔY1) and (ΔY2) are the weight losses of moistureand HCl, respectively; M1 and M2 are the molecular weights of aniline and HCl, respectively; and X isthe number of aniline repeating units. Therefore, according toEq. (1), I substituted ΔY1, ΔY2, M1, and M2with 10, 18, 92, and 63, respectively. Then, weobtained the value of X at around 2.74. This implied that there were roughly 2.8 aniline repeat units, on average, doped with 1 HCl molecule in the ES-PANI form.Fig 5 shows the TGA results of the EB-form andES-form PANI powders under a N2 atmosphere. Forthe EB-form, there were two major stages for the weight loss of the PANI sample. The firstweight loss, at around 100°C, resulted from the evaporation of moisture, which was consistent with theDSC result [15].The second weight loss, at the higher temperature, indicated chemical structure degradation of the PANI molecule; the degradation temperaturewas around 400–450°C. For the ES-PANIpowder, there were three major stages for weight loss, around 100, 200, 360 and 410°C, which were assigned to the removal of moisture, HCl, and the degradation of the PANI molecule, respectively. This apparently indicated that the degradation temperature of the EB-PANI was higher than that of ES form. This may have been caused from the HCl, gas formed during the heating process; this strongacid vapor accelerated the degradation of the ES-PANI. Also, this showed that the moisturecontent of the ES-PANI powder was higher than that of the EB form, as shown in Fig 5.

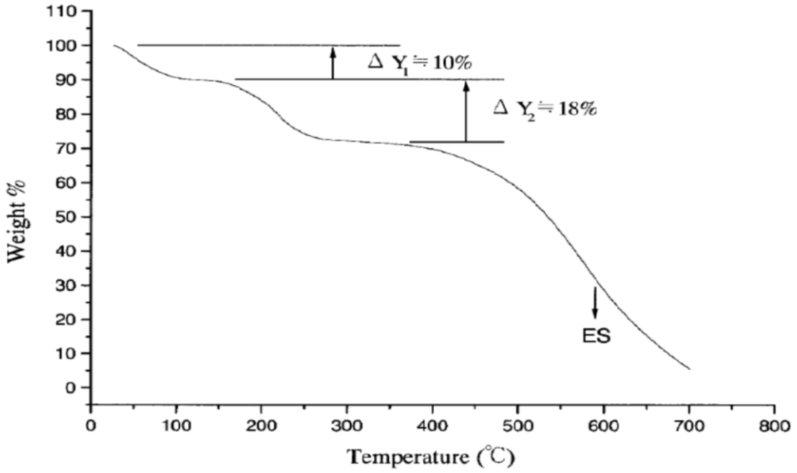


Figure 5.TGA curve of ES-doped PANI powder under aN_2gas (heating rate ~20°C/min).

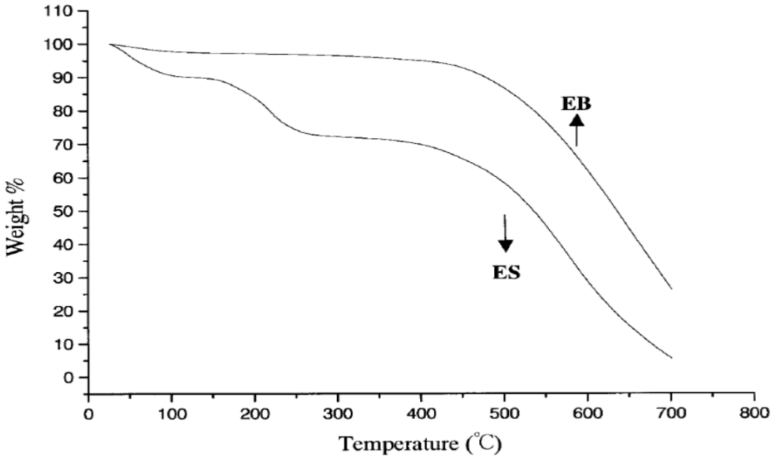


Figure 6.TGA curves of EB and ESform PANI samples under N_2gas (heating rate ~ 20°C/min).

VI. CONCLUSION

FESEM images indicated that the particle size of the polymer within the micro-scale and with the presence of acid. The XRD results showed that the EB-PANI had a small amount of crystallinity. However, the annealed EB-PANI powder sample (at 250°C for 1h), there was only a broad amorphous nature as semi-crystalline structure. This phenomenon again illustrated that if the thermal energy was high enough, the chemical crosslinking reaction occurred among the EB-PANI polymer chains. The polarizing micrograph of the crystalline EB-PANI was successfully revealed. We found the single and the more complex multi-layered branched crystalline morphologies of the EB-PANI. DSC thermal analysis curves indicated that the EB-PANI had discernible moisture content. This phenomenon was in agreement with TGA results. Moreover, at the first run of the DSC thermal analysis, an exothermic peak around 170–340°C was found. This peak was due to the chain crosslinking, resulting from a coupling of two neighboring -N=Q=N- groups to give two -NH-B-NH-, groups through a link of the N with its neighboring quinoid ring. The FTIR examinations further confirmed the chemical crosslinking reaction among the pure polymer chains. TGA results illustrated that the degradation temperature of the EB-PANI powder was around 450°C. Also, from the TGA curve of the ES-form PANI, we calculated that 2.74 aniline repeating units, on average, doped with HClacid.

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