

Chapter- 2

Experimental Details

2. Experimental Details

2.1 Materials procurement and WPCB's pre-processing

Nearly 50 kg of the Waste Printed Circuit Boards (WPCBs) generated from motherboards of computers were collected from local e-waste scrap collectors. All the WPCBs were cleaned with hot water (60-70 °C) and acetone baths to free them from any dirt, grease, and other contaminations. Mild heat-assisted (using heat gun) manual separation/detachment of mounted electronic components (resistor, integrated circuits, capacitor, relay, transformer and ram/processor slot etc.) was carried out by plier. The temperature of heat gun was limited to 200 °C because solder melts near 180-190 °C and enables easy detachment of solder. The solder metal was collected separately and the bare WPCBs were chopped into different sizes (20.25 cm², 16 cm², 12.25 cm², 9 cm², 6.25 cm², 4 cm², 2.25 cm² and 1 cm²) by using a handheld shear cutter. The overall flow sheet of pre-treatment of WPCBs is shown in **Figure 2.1**. All chopped WPCBs were well rinsed twice with hot distilled water and acetone to remove any dust, grease, chemical, adhesive, smudge etc. and dried for 24 h at room temperature then kept in a desiccator.

Various analytical grade reagents used in the present investigation were: Acetone (Fisher Scientific, India), dimethylformamide (Sisco Research Laboratories, India), dimethylacetamide (Sisco Research Laboratories, India), bisphenol-A (Sisco Research Laboratories, India), pure ethanol (Fisher Scientific, India), deuterium-chloroform (CDCl₃-d) (Sigma-Aldrich Corp.), potassium bromide (Sigma-Aldrich Corp.), Sulphuric acid (Fisher Scientific, India), Nitric acid (Molychem India Pvt. Ltd.) and Hydrogen peroxide (Fisher Scientific, India). The various physical and chemical properties of DMF and DMA are listed in **Table 2.1**.

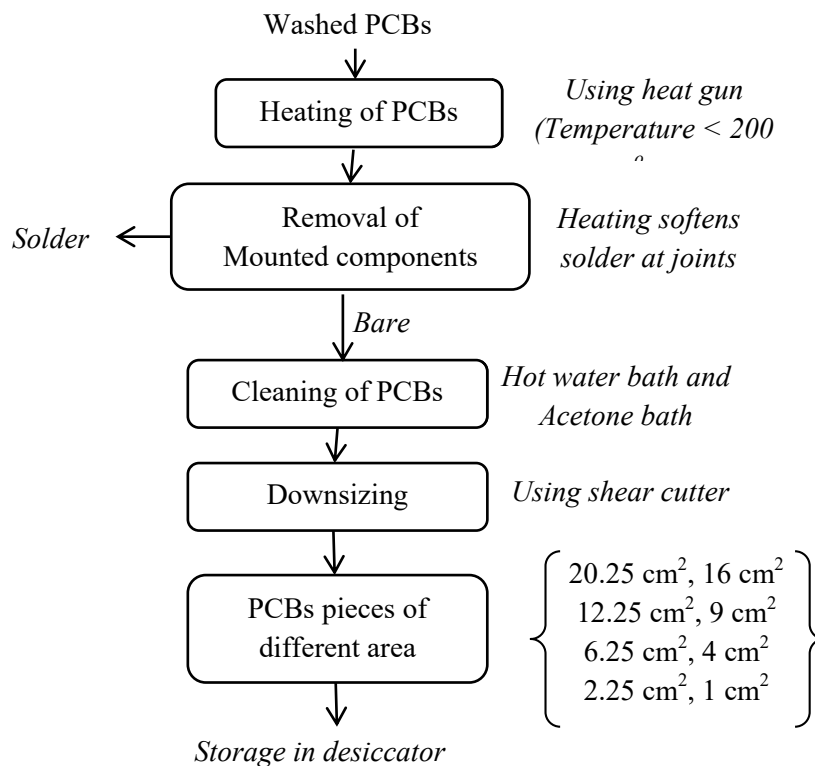


Figure 2.1- Flow-sheet showing the mechanical pre-processing of WPCBs

Table 2.1- Various properties of DMF and DMA

Properties	DMF	DMA
Chemical formulae	C ₃ H ₇ NO	C ₄ H ₉ NO
Molar Mass (g·mol ⁻¹)	73.10	87.12
Molar volume (mL·mol ⁻¹)	77	93
pH (20% solution, 20 °C)	6.7	4
Boiling Point	153-154 °C	164-165 °C
Specific Heat (J·K ⁻¹ ·mol ⁻¹)	120	178.2
Density (g·mL ⁻¹)	0.9445	0.937
Viscosity (cP)	0.802	0.92
Dielectric constant (at 10 kHz)	36.7	37.8
Vapor pressure (mm Hg)	3.87	2
Dipole moment (C·m at 20 °C)	1.27 × 10 ⁻²⁹	3.79 × 10 ⁻²⁹

all properties at 25 °C

2.2 Estimation of composition of WPCBs

The chopped WPCBs were crushed to -1 mm size by using hammer mill make *Ikon Instruments, India* and chemical composition was determined by using Atomic Absorption Spectrophotometer (AAS) make *Elico SL 168, India*. For analysis, 10 g of WPCBs were digested in freshly prepared aqua regia ($3\text{HCl}:1\text{HNO}_3$) at $80\text{ }^\circ\text{C}$ for 1 h. The aqua regia was poured into a three-neck flask and heated to pre-set temperature. Once the temperature is attained, the WPCB powder was slowly added into the reaction flask from sampling mouth. The central opening was used to install a condenser for condensing any vapour escaping the system. Continuous heating and stirring were provided by an automatic ceramic top hotplate cum magnetic stirrer (temperature accuracy $\pm 1^\circ\text{C}$). The schematic view of the setup used for digestion is shown in **Figure 2.2**.

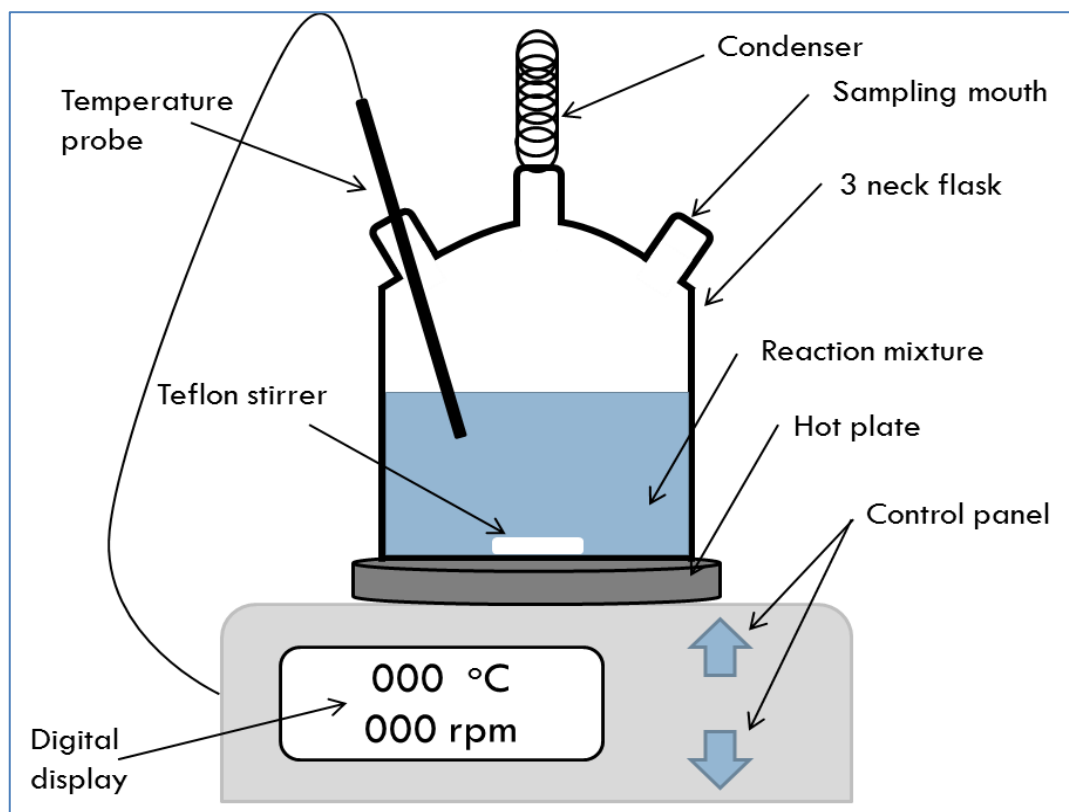


Figure 2.2- Schematic view of the experimental setup used for digestion

After dissolution, the slurry was filtered by filter paper (Whatman No. 42) using a vacuum filtration assembly. After digestion, the residue was obtained which is supposed to be having a large fraction of non-metallic material because it does not react with aqua-regia. The undissolved residue was weighed to obtain satisfactory mass balance and then disposed of properly. The pregnant liquor containing metal ions was adequately diluted by adding distilled water. The metal content was determined by AAS against a known set of standard solution of respective metal ions by using hollow cathode lamp of copper operating at a wavelength of 324.8 nm. A quartet of digestion experiment was performed with random samples of WPCBs to estimate the average composition. The results showed that WPCBs contains 22 wt% copper along with considerable fractions of gold and silver (**Table 2.2**).

Table 2.2- Average metal composition of WPCBs

Element	Wt%
Cu	22.3
Zn	0.606
Ag	0.001
Au	0.0002
Fe	0.35
Non-metal	70% (undissolved fraction)

2.3 Estimation of decomposition temperature of WPCBs

Thermogravimetric Analysis (TGA) of WPCBs powder (-1 mm) was carried out to understand the effect of temperature on the decomposition. The TGA analysis was carried out on the *Cahn Balance (Thermo Microbalance-D101)*. Nearly 1.2 g of WPCB powder was kept in a silica crucible and mounted on the sample holder end of Cahn balance. The balance was kept in the stabilization mode for 12 h and then the gas flow

was started at a constant flow rate of $3 \text{ L}\cdot\text{min}^{-1}$. The experiments were carried out using nitrogen (inert) and hydrogen (reductive) gases. After 30 min of gas flow, the heating was started and material in the crucible was heated to $450 \text{ }^\circ\text{C}$ in a vertical tube furnace at a constant heating rate of $4 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The controller of the balance recorded the change in weight of samples with respect to time and temperature. After the completion of the experiment, the furnace and controller were switched off while the flow of gases was kept on to avoid the contamination of the hot sample by atmospheric gases. After reaching the room temperature, the gas flow was stopped and the sample with crucible was carefully unmounted. The thermally treated WPCBs samples were weighed and the satisfactory mass balance was obtained. The TGA results in hydrogen and nitrogen atmosphere are shown in **Figure 2.3**.

The result shows that initially, the WPCBs is unaffected by the applied temperature up to $90 \text{ }^\circ\text{C}$. Later, the rise in temperature $120 \text{ }^\circ\text{C}$ led to minor weight loss. This may be because of the vaporization of moisture content which may have been associated with WPCBs during the processing or due to the increased surface area after pulverization. In case of nitrogen and hydrogen, similar results were seen up to $120 \text{ }^\circ\text{C}$. Results showed a similar trend of weight loss in nitrogen and hydrogen atmosphere up to $120 \text{ }^\circ\text{C}$.

A. TGA analysis in nitrogen atmosphere

The slope of the curve is zero in $120\text{-}300 \text{ }^\circ\text{C}$ indicating no evidence of decomposition. Further rise in temperature showed steep weight loss up to $380 \text{ }^\circ\text{C}$ and later the rate of weight loss again decreased (**Figure 2.3**). The results also showed that total weight loss is in order of 30%. The WPCBs comprise of organic compounds which dissociates to lower molecular weight products at high

temperature. Thus, using nitrogen major weight loss has been experienced in 300-380 °C range.

B. TGA analysis in hydrogen atmosphere

The usage of hydrogen showed a similar trend of weight loss in 280-360 °C. Major weight loss of 28 wt% has been registered in the above temperature range. It may be interpreted that that hydrogen results in decomposition of WPCBs in lower temperature range relatively. This may be due to the fact that hydrogen is a reducing gas.

These studies showed that organic fraction of WPCBs is decomposed in 280-380 °C and thus, WPCBs may be processed safely at higher temperatures in the range of 200 °C without risk of decomposition. These results are also in good agreement with the results reported in the literature [125,127,134].

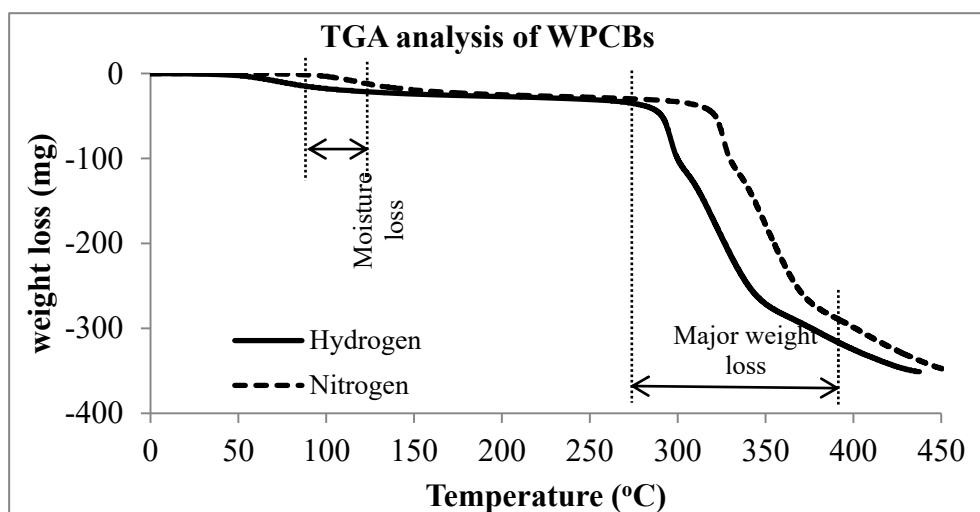


Figure 2.3- Thermal degradation profile of WPCBs in different atmosphere

2.4 Downsizing of WPCBs by Hammer milling

The downsized WPCBs of size 2.25 cm² were crushed to -1 mm by using hammer mill make- *Ikon Instruments, India*. The hammer mill with its different parts is shown in

Figure 2.4. The chopped WPCBs were fed into the inlet chute of hammer mill at specific feed rates. The material was crushed by the simultaneous impacts exerted by the four swinging hammers (mounted on the drive shaft) till the size is reduced to -1 mm. The crushed material is passed through a perforated screen having an opening of 1 mm placed in the bottom side of crushing chamber. The milled WPCBs were collected from the outlet chute.

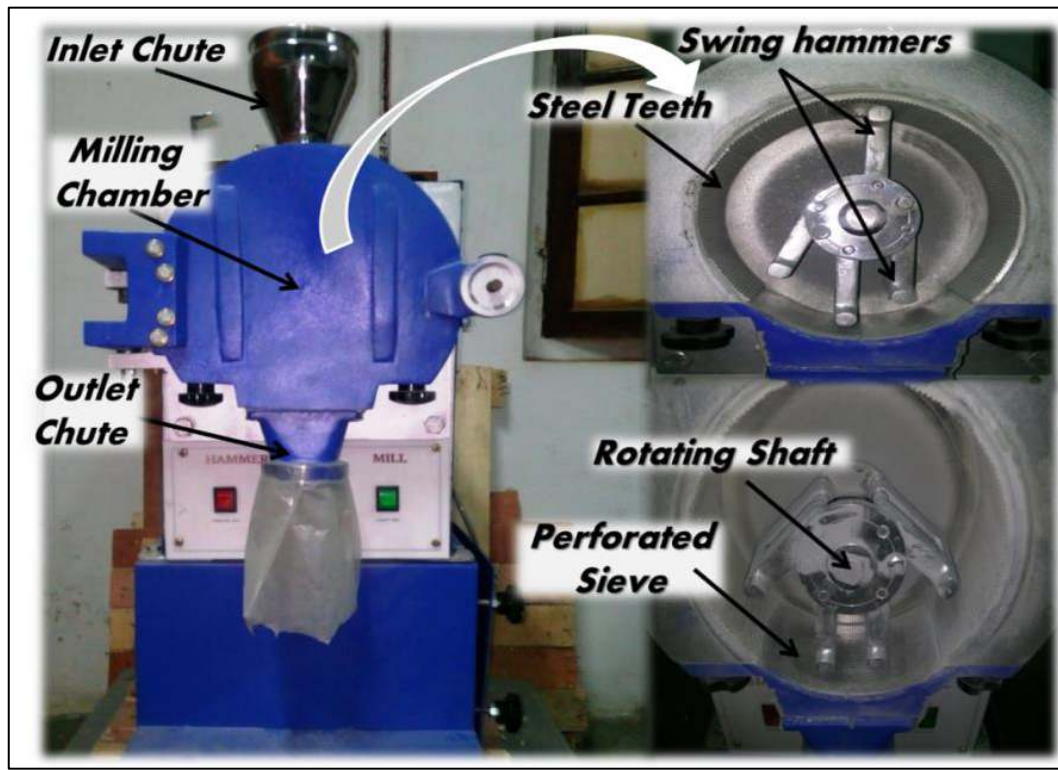


Figure 2.4- Hammer Mill and its milling chamber

The effect of milling time and feed rate on the grinding of WPCBs has been studied to obtain optimum milling parameters. The different milling times were chosen *viz.*, 30 sec, 1, 1.5, 3, 5, 7 and 10 min; and the feed rates were varied as- 3, 8 and 12 $\text{kg}\cdot\text{h}^{-1}$. After the crushing, the sieve analysis carried out to study the particle size distribution. The sieve analysis has been carried out by a vertical Sieve Shaker having series of nine test sieve *viz.*- ASTM 18, 30, 35, 50, 70, 100, 120, 140 and 230. These test sieves were

arranged in descending order of aperture from top to bottom. The aperture size of individual sieve has been shown in **Table 2.3**. After 15 min, the shaker was turned off and particles accumulated in various sieves have been collected and weighed by using a digital weighing balance.

Table 2.3- Test- sieves used for the analysis of the milled WPCBs

ASTM No.	Sieve aperture (mm)	Size of retained fraction (mm)
18	1	+ 1
30	0.6	-1 + 0.6
35	0.425	-0.6 + 0.425
50	0.3	-0.425 + 0.3
70	0.212	-0.3 + 0.212
100	0.15	-0.212 + 0.15
120	0.125	-0.15 + 0.125
140	0.106	-0.125 + 0.106
230	0.063	-0.106 + 0.063

To estimate the amount of copper in different size fractions, 0.5 g of respective sample was digested in aqua-regia as mentioned in **Section 2.2**. After digestion, excess acid was evaporated and the digested liquor was diluted to 50 mL by adding distilled water. The diluted samples were analyzed by AAS. Microscopic examinations of milled WPCBs were carried out by using optical microscope at 10X magnification to observe the morphology of milled WPCBs particles. The Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis was of milled WPCBs after 7 min were also carried out to observe surface morphology and quantitative composition of

individual particles. The SEM was performed on instrument make 'Zeiss Evo-18 Research 2045' with EDS attachment make 'Oxford X-act INCAx-act'.

2.5 Dissolution of HER of WPCBs in organic solvent(s)

The HER dissolution experiments were performed into a wide mouth, round bottom type flanged head borosilicate glass reaction vessel of 1 L capacity make 'Borosil Glass Pvt. Ltd. India (Cat No- 4330029)'. The vessel was covered by the detachable head having three necks. A Graham coiled distillate type condenser of 30 cm effective length was installed in one neck to recover any escaping vapour. The flask was mounted inside an electrically operated heating mantel with a digital temperature controller with an accuracy of ± 1 °C. The **Figure 2.5** shows the schematic view of the setup used for dissolution of HER. The measured quantity of solvent (DMF/DMA) was poured into the flask through sampling neck and heated to preset temperature. Then, the requisite amount of WPCBs was charged into the vessel to maintain desired WPCB to the solvent ratio (wt/vol). The temperature was maintained by a sensor connected to an automated proportional-integral-derivative (PID) controller inserted from 3rd neck (placed inside a glass pocket filled with mercury dipped in the solvent). Agitation during the experiment was provided by Teflon blade stirrer at 150 rpm to eliminate mass transfer effect on dissolution. To study the progressive dissolution of HER, 1 mL of the solvent from the reaction mixture was withdrawn after a time interval of 15, 30, 60, 90, 120, 150, 180 and 240 minutes. Once the experiment is over, the 'solvent(s) treated WPCBs' were separated by filtration using filter paper (Whatman No. 42) and rinsed twice with hot distilled water and acetone bath. After the treatment by solvent(s) evidence of delamination of layers of WPCBs were seen. A digital camera make 'HTC One_M8' recorded the evidence of cracking and delamination. The pregnant solvent was also

stored for the subsequent processing. Washed WPCBs were dried at 80 °C for 8 h and then kept into the desiccator. Triplicate of experiments were performed to observe the reproducibility of obtained results and minimize the effect of random instrumental errors. The mean values of the sum of dissolved HER with error bar have been reported. Initially, all the experiments were carried out to optimize HER dissolution in solvent DMF. The varying parameters chosen for study were: WPCBs(g):DMF(mL) ratio – 0.5:10, 1:10, 1.5:10, 2:10, 3:10, 3.5:10 and 4:10; Temperature – 80, 110, 135, 155 °C; fed WPCBs size – 1, 4, 9 and 16 cm². Later, experiments by using DMA were carried out for optimized dissolution of HER. The investigated parameters were: WPCBs(g):DMA(mL) ratio – 1:10, 2:10, 3:10; Temperature – 120, 140, 160 °C; fed WPCBs size – 1, 4 and 9 cm². The optimized conditions for maximum HER dissolution were found to be different in both cases and to evaluate the relative effectiveness of these solvents, experiments under similar parameters were also performed. The experimental condition chosen for comparative study were: WPCBs(g):solvent(mL) ratio – 1:10, 2:10, 3:10; Temperature – 120, 140 °C; WPCBs size- 2.25, 6.25, 12.25 and 20.25 cm².

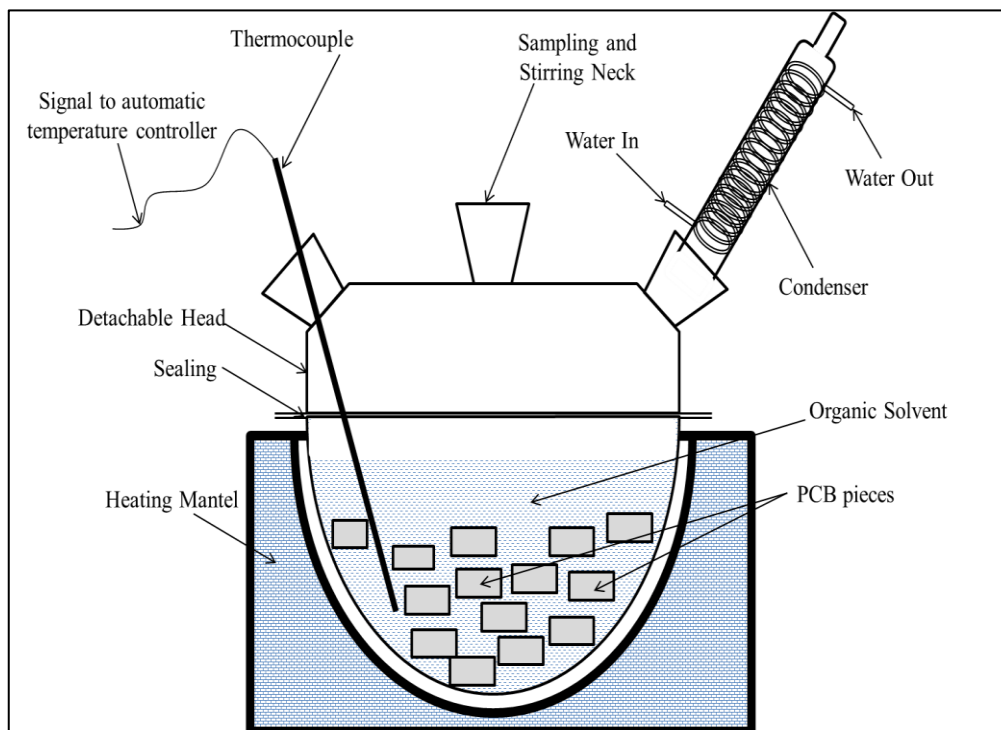


Figure 2.5- Schematic view of experimental Setup for dissolution of HER

2.6 Analysis of dissolved HER in organic solvent(s)

The HER is formed by curing di-glycidyl ether of bromine substituted bisphenol A (BPA) with suitable hardener [222]. The curing results in the formation of a polymeric chain of bisphenol-A (BPA) linked together by ethers (**Figure 2.6**) [223,224]. Thus, quantification of BPA helps in the estimation of HER dissolved in the solvent(s).

Thus, HER dissolved in the solvent(s) was quantified by Ultraviolet-visible spectroscopy (UV-VIS) against the concentration vs. absorbance curve plotted for pure BPA. BPA shows maximum absorbance against UV light of wavelength 282 nm and this technique is well established and validated for analysis of dissolved HER in ionic/organic solvents [202,206,207,209,224,225]. To plot concentration vs. absorbance curve for BPA, a stock solutions of $2000 \mu\text{g}\cdot\text{mL}^{-1}$ BPA (0.2 g pure BPA dissolved in 100 mL ethanol) was diluted with pure ethanol to prepare standard solutions of 4, 5, 8, 10, 12,

15, 16, 20, 24, 25, 28, 30, 32, 35, 36, 40, 44, 45, 48, 50, 52, 55, 56 and 60 $\mu\text{g}\cdot\text{mL}^{-1}$ BPA concentrations. The absorbance of the standard solutions was measured on 'Perkin Elmer-XLS Plus' spectrophotometer with 1 cm matched quartz cuvette. The absorbency data with varying concentration of BPA is shown in **Figure 2.7**.

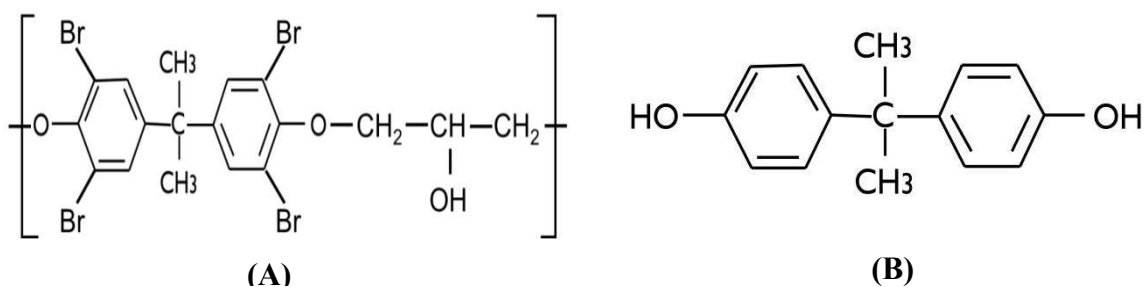


Figure 2.6 – Chemical structure of (A) polymer chain of halogenated epoxy resin; (B) BisPhenol-A

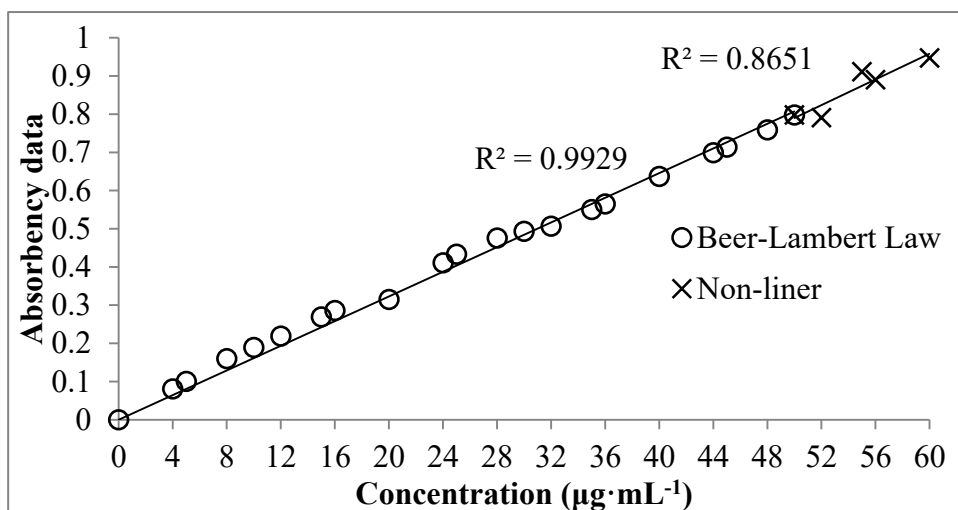


Figure 2.7 - Absorption curve for varying concentration of BPA

The absorbency data revealed excellent curve fitting with R^2 values of 0.9929 up to 50 $\mu\text{g}\cdot\text{mL}^{-1}$, and later the data does not shows a good fit. This indicates that Beer-Lambert law is applicable only up to 50 $\mu\text{g}\cdot\text{mL}^{-1}$ BPA concentration. So, in order to estimate the

concentration of HER in the representative samples and pregnant solvent(s) against the standard curve, adequate dilution was done by pure ethanol.

2.7 Recovery of spent solvent and its analysis

The pregnant solvent(s) obtained after separation of ‘solvent treated WPCBs’ was subjected to regeneration by using the high vacuum decompression rotary evaporator condenser unit. The regeneration left back two products *viz.*, regenerated solvent(s) and recovered residue. Both DMA and DMF are commercial solvents used in numerous application and many times these can be recycled by evaporation and condensation. Thus, in the present study, significant efforts have been devoted in analyzing the chemical structure of regenerated solvent(s) by different analytical techniques like-Proton and Carbon nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$), Fourier transform infrared spectroscopy (FT-IR), TGA-differential thermogravimetric (DTG), Gas chromatography (GC), ASTM boiling point estimation. The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ analysis of regenerated solvent(s) and pure solvent(s) had been carried out on ‘*Bruker ASCENDTM 500 NMR*’ to study the respective positions of hydrogen and carbon atoms in the molecular structure. The NMR analysis was carried out after pouring a mixture of 0.5 mL of liquid sample and 4.5 mL of $\text{CDCl}_3\text{-d}$ into a 5 mm diameter and 500 MHz compatible NMR tube. The FT-IR analysis of pure solvent(s) and the regenerated solvent(s) had been carried out on ‘*Shimadzu FT-IR 8400S*’ by placing 0.2 mL of the liquid sample homogenously spread as a thin layer between two sodium chloride cuboids. The TGA-DTG of the liquid sample was carried out on ‘*Thermo Recording Balance D101*’ by placing 0.5 g of solvent in a silica crucible and heating it to 225 °C at a rate of 10 °C·min⁻¹ in the nitrogen atmosphere. The GC analysis was carried out on ‘*NUCON 5765*’ gas-chromatograph by using flame ionization detector

(FID) with an SE-30, 10% chromosorb tungsten packed stainless steel column (2m × 2mm). Nitrogen was used as a carrier gas at the rate of 40 mL·min⁻¹. The oven column temperature ranged from 70 to 230 °C; programmed at 7 °C·min⁻¹ with initial and final hold time of 10 min. Injector and detector temperatures were 220 °C and 230 °C, respectively. The injection volume was 0.02 L with split ratio 1:30. The percentages of the individual constituents were calculated by electronic integration of the FID peak areas without response factor correction. The regenerated solution(s) was subjected to measurement of initial boiling point as per ‘ASTM D86’ standard method [226,227]. To estimate the efficiency of regenerated solvent(s) to dissolve HER, it was subjected to multiple cycles of dissolution and regeneration. After each cycle, the loss in the volume of solvent(s) was also recorded.

2.8 Analysis of recovered residue

After the regeneration, dissolved materials were also recovered as residue, and it was crushed to fine particles by using mortar and pestle. The UV-VIS study of pregnant solvent(s) showed the presence of BPA which is a major constituent of HER chain. Thus, it has been anticipated that the recovered residue may contain polymeric material of HER and solder mask. In order to validate the pre-assumed hypothesis, the residue, untreated HER and BPA were subjected to FT-IR studies. The FT-IR spectra were recorded by ‘Perkin Elmer FT-IR spectrum 2’ spectrophotometer after pressing the homogenous mixture of 1 mg sample with 100 mg of potassium bromide (KBr) in a transparent sheet in accordance with standard KBr pellet method. The untreated HER was collected from bare WPCBs by manual scratching using a sharp blade. The quantitative chemical composition and morphology of the recovered residue and untreated HER were examined by SEM-EDS analysis. The TGA-DTG analysis data of

recovered residue were also recorded on 'Mettler Toledo TGA/DSC 1' by heating the samples up to 500 °C at a heating rate of 10 °C·min⁻¹ in the nitrogen environment after placing it into an alumina crucible.

2.9 Mechanism of interaction of solvent with WPCBs

The mechanism of the dissolution of HER in the solvent has also been studied to better understand the dissolution process. So, one HER dissolution experiment in solvent DMA was carried out for 8 h as mentioned in section 2.5. The conditions chosen were: 3:10 WPCBs:DMA ratio, temperature 160 °C and fed WPCBs size- 1 cm². The representative samples were withdrawn after 1, 2, 3, 4 and 8 h of contact. The molecular array and structure of representative samples were analyzed by NMR and FT-IR analysis as mentioned in Section 2.7.

2.10 Comparative study on leachability of copper form solvent treated and hammer milled treated WPCBs

After the optimized dissolution of HER, WPCBs were completely separated into layers. This ensures complete liberation of copper laminates. It is also reported in the literature that milling does not result in complete liberation of metal values. Thus, investigations were carried out to find the relative effectiveness of WPCBs pre-treatment by solvent on the leachability of copper. The leaching of copper from 'solvent treated WPCBs' and hammer milled WPCBs (-1 mm) were carried out in a 100 mL capacity Teflon shell type hydrothermal autoclave bomb make: *Shilpend, Model: Auto100X*. The schematic diagram of the reactor bomb is shown in **Figure 2.8**. In a thesis [228] improved copper leaching from 1 cm² size WPCBs has been reported under hydrothermal condition *viz.*- sulphuric acid concentration - 3M, pulp density 50 g·L⁻¹, temperature 140 °C and time 3 h as compared to atmospheric leaching. The reported conditions were chosen in the

present study and leachability of copper has been investigated in presence of varying concentrations of oxidants viz., hydrogen peroxide (H_2O_2) and nitric acid (HNO_3). During the experiments, 60 mL of leachant ($3\text{M H}_2\text{SO}_4 + \text{oxidants}$) was poured into the hydrothermal bomb and ‘solvent treated WPCBs’ were also fed to maintain pulp density of $50 \text{ g}\cdot\text{L}^{-1}$. Experiments with varying concentration (5%, 10% and 15%) of oxidants were performed. The shell cover (Teflon), spring and pressure plate of the bomb were placed on the top and tightened by using screw cap (**Figure 2.8**). After that, the reactor bomb was placed in a muffle furnace which was maintained at $140 \text{ }^\circ\text{C}$. The initial 30 min were consumed by the reactor bomb to reach preset temperature and next 75 minutes was the constant temperature reaction time. The leaching experiments were further extended to study the behaviour of copper dissolution from WPCBs concentrate obtained after hammer milling and sieving. After the completion of the reaction, the furnace was switched off; reactor bomb was taken out and cooled quickly by the water bath. Once the reactor was cooled down it was disassembled and the slurry was filtered by vacuum filtration using filter paper (Whatman No. 42). The leached residue was dried in an oven at $80 \text{ }^\circ\text{C}$ for 4 h; and after drying, the satisfactory mass balance was obtained. The leach liquor was diluted with distilled water and concentration of copper was analyzed by AAS as mentioned in **Section 2.2**. The X-ray diffraction (XRD) analysis of leached residue, hammer milled WPCB concentrate, crushed copper laminates of ‘solvent-treated WPCBs’ were performed to observe the various phase(s) present. The XRD of the sample has been recorded by using ‘*Rigaku Miniflex Dtex Ultra 600*’ diffractometer. The morphology, quantitative composition and nature of distribution of the elements present in the leached residue, hammer milled WPCB concentrate, crushed copper laminates of ‘solvent-treated WPCBs’ has also been examined by SEM-EDS analysis. This analysis was carried out on SEM make

'TESCAN, VEGA-3, LMU' having the EDS attachment 'Oxford, X-ACT, Penta FET Precision'.

2.11 Recovery of solder material during the pre-processing of WPCBs

During the pre-processing of the WPCBs, mild heating was carried out to easily detach the mounted components. The solder material is used to attach the components on the WPCBs and thus, during pre-processing the solder material has been also recovered (Figure 2.9). After preprocessing of 50 kg of WPCBs ~ 2 kg solder has been recovered.

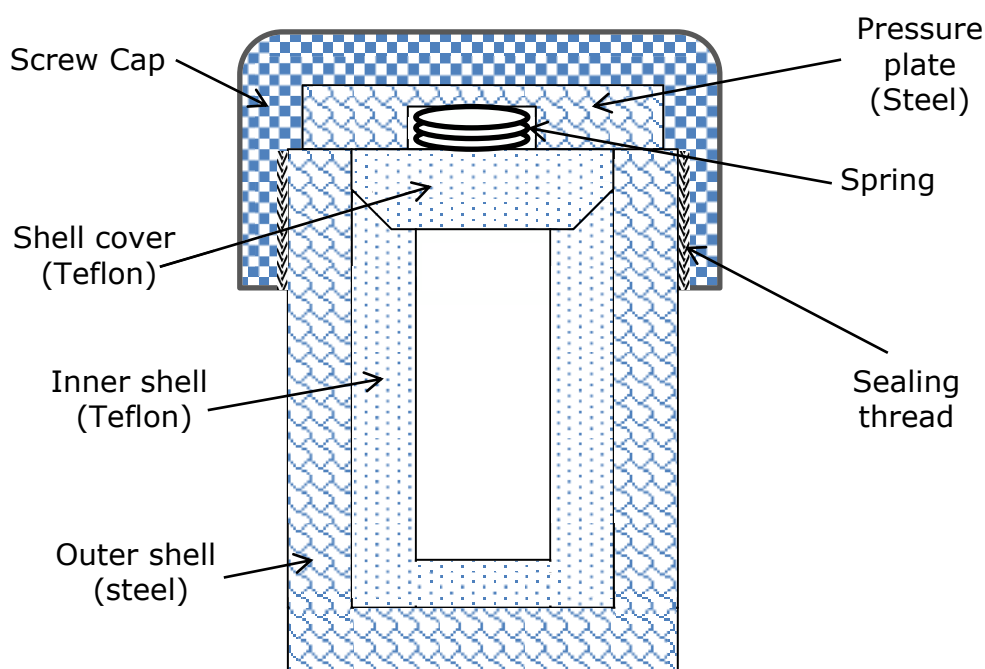


Figure 2.8- Schematic diagram of hydrothermal autoclave bomb used for leaching of copper



Figure 2.9- Solder material collected during the pre-processing