PREFACE

This research work embodies the investigation carried out on the delamination of Waste Printed Circuit Boards (WPCBs) pieces of varying size by using the organic solvent(s)- *Dimethylformamide* (DMF) and *Dimethylacetamide* (DMA). The PCBs are manufactured by sandwiching the layers of glass fibre and copper clad by using Halogenated Epoxy Resin (HER) as a reinforcing agent. In the present work, significant dissolution of the HER has been achieved for WPCBs of different sizes. The present study is mainly focused on the development of a cost-effective and eco-friendly technique having the capabilities of delamination of WPCBs and efficient liberation of metal clad of WPCBs. The leachability of copper after organic solvent treatment and conventional treatment has also been considered to justify the relative merits of proposed process. The conventional liberation of metallic values by using hammer mill, has also been optimised. The efficient and economical liberation of metal clad of WPCBs will eventually result in-economic viability of hydrometallurgical recycling and thus, development of a commercial WPCB recycling technique.

It is evident from the literature review that there are two major routes for recycling of WPCBs *i.e.,* thermal and hydrometallurgical route. All existing thermal process results in complete destruction of the organic constituent of WPCBs and that leads to emission of dioxins, furans, acid vapour, and unsaturated hydrocarbons. These emissions are extremely lethal and due to stringent environmental protection laws these processes have not been yet commercialized. Alternatively, WPCBs recycling by hydrometallurgical route is having no emission, and high metal recovery yield. However, the economy of hydrometallurgical process is still debatable due to inclusion of pre-treatment of WPCBs. The pre-treatment ensures successful liberation and separation of metal form non-metal encapsulated structure. Without pre-processing, consequences *viz.,* excess leachant consumption, high effluent generation, low metal recovery yield etc. are exerted. Further, only 75-80% metal liberation and separation is practically achieved. In addition, loss of precious metal in dust, noise pollution, high energy needs etc. of pre-processing pushed the researchers to look for an eco-friendly and economical alternative.

In view of above, an economical and eco-friendly technique has been explored. It results in successful liberation of metal clad, thus it is possible to recover metal values completely.

The scope of the present work is as follows:

A. Chemical composition study of WPCBs; conventional treatment by hammer milling and optimization of milling parameters to achieve maximum metal liberation.
B. Study of delamination of WPCBs in solvent DMF and DMA, and optimization of parameters.
C. Comparative study of liberation of metal clads in both solvent and study of delamination of large size WPCBs in relatively better solvent system.
D. Studies on the recycling of used solvent and recovery of dissolved HER for safe disposal. Estimation of the effect of recycling of solvent on subsequent dissolution.
E. Investigation on the effect of leachability of copper after conventional pre-treatment and solvent treatment.

F. Exploration of the governing mechanism responsible for the dissolution of HER in the solvent and with scientific evidences.

The proposed work has been subdivided into four chapters and references have been indexed after scope of future work. The results obtained from this work have been divided into five major sections.

The background representing the WEEE introduction, importance, generation and present recycling status has been discussed in the **first chapter**. The detailed discussion of the various techniques which have been exercised for the WEEE recycling has also been incorporated. This chapter also focuses on the major hurdles being faced during the recycling and the background of our proposed research work. This chapter describes the motivation of our present research work.

The **second chapter** gives the detailed overview of our research strategy, approach and experimental details. The WPCBs collection and its mechanical processing have been discussed in this chapter. The major points which have been clubbed in this chapter are indexed below-

a. Sources explored for the collection of WPCBs and its mechanical processing.
b. The chemical composition of WPCBs by a relevant technique that showed the presence of 22.3% copper.
c. Details of hammer milling process of WPCBs, parameters chosen for study and details of sieve analysis of milled WPCBs.
d. Experimental details of dissolution of HER in solvent DMA and DMF and study of the effect of governing parameters of dissolution. The approach explored the recycling of the solvent after usage, and recovery of HER

e. The details of leaching experiments of copper dissolution have been indexed in this chapter and the brief methodology of the study of the HER dissolution mechanism in the solvent has also been indexed in this chapter.

The **third chapter** includes detailed results and discussion relevant to the present study. It has been divided into 5 subsections *viz.,*

1. Section 1- Hammer milling of WPCBs and optimization of parameters
2. Section 2- Delamination of WPCBs by dissolution of HER in DMF
3. Section 3- Liberation of WPCB's metal-laminates by HER dissolution using DMA
4. Section 4- Comparative study of HER dissolution in DMF *vs.* DMA and its mechanism
5. Section 5- Delamination of large size WPCBs and post-treatment leaching of copper

1. Hammer milling of WPCBs and optimization of parameters

Pre-hammer milling, the study of the thermal decomposition of WPCBs showed that it decomposes in the temperature range of 260- 380 ^{o}C. Study of the effect of milling parameters showed that after 7 min, 94% of fed WPCBs are milled to -1 mm. Size distribution results also showed that-

a. 30% crushed particles are in -0.063 mm size
b. 50-55% milled particles are in +0.15 mm size
c. +0.15 mm fraction contains 43% copper by weight
d. 83-87% of the original copper content of WPCBs has been concentrated in +0.15 mm.

Microscopic examination of -1 mm size milled WPCBs showed that copper is in form of a thin sheet, while glass particles possess bamboo like fibrous structure.

2. Delamination of WPCBs by dissolution of HER in DMF

Study of dissolution of HER in DMF showed that higher temperature, WPCB:solvent ratio, and lower size of WPCBs favours dissolution. The most efficient HER take up in DMF has been achieved for WPCBs of 1 cm^2 size under 135 ^oC, 4 h, WPCB:DMF- 3:10. After, HER dissolution the layers of WPCBs were separated and metal clad were liberated.

The used solvent has been recycled by rotary compression evaporation and it has been successfully validated by NMR and FT-IR analysis. The results also revealed that regeneration even after 5 times doesn't affect the HER take-up capabilities.

The dissolved solute was recovered during regeneration and its SEM-EDX and FT-IR analysis revealed that it is HER.

3. Liberation of WPCB's metal-laminates by HER dissolution using DMA

The study of governing parameters of HER dissolution on DMA showed the similar effect as registered in case of DMF. Using DMA, most efficient HER dissolution has been experienced for 1 cm^2 size WPCBs under 160 ^oC, 3 h, WPCB:DMA- 3:10. DMA treatment also resulted in complete delamination of layers of WPCBs along with the dissolution of inert 'Solder mask' layer.

After the dissolution, spent DMA was subjected to regeneration and subsequent Initial boiling point analysis, NMR, FT-IR, TGA-DTG and GC analysis revealed that DMA is entirely recyclable with very high purity. It is also found that after each regeneration cycle, 3-5% DMA loss is exerted that may have been consumed in the wetting of glass, WPCB and other contact surfaces.

The dissolved solute was recovered as in the case of DMF. Further, SEM-EDX, FT-IR and TGA-DTG analysis of residue confirmed that it is the HER only.

4. Comparative study of HER dissolution in DMF vs. DMA and its mechanism

Both solvents resulted in the dissolution of HER and delamination of WPCBs. The optimized conditions were different for both solvent and thus, a comparative study has been carried out under common parameters. Comparison of the properties of both solvents showed that DMA possesses higher molar mass, boiling point, specific heat, dielectric constant, dipole moment and low vapour pressure. Variation in these properties indicates that DMA is probably better solvent for dissolution of polar solutes like- HER. Further, experiments using DMA and DMF under varying parameters *viz.*- WPCB size (2.25, 6.25, 12.25, 20.25 cm^2), WPCB:solvent (3:10, 2:10, 1:10) and temperature (140, 120 ^oC) were carried out. The studies proved that DMA is relatively better by dissolving 77% more HER for 2.25 cm^2 size WPCBs.

In order to understand the dissolution mechanism, detailed NMR and FT-IR analysis of representative samples were carried out. Representative samples were withdrawn after 1h, 2h, 3h, 4h, and 8h of the reaction of DMA with 1 cm^2 WPCBs under 160 ^oC, WPCB:DMA of 3:10. The NMR analysis of all representative samples showed shift of hydroxyl group of HER towards a higher frequency. Further, FT-IR analysis of all representative samples showed a shift of hydroxyl peak of HER and carbonyl peak of DMA to lower frequency. These shifts confirms H-bond formation between HER and

DMA. The shift of proton donor group (105 cm^{-1}) was more dominant than proton acceptor moiety (13 cm^{-1}) which further corroborates with the H-bond formation results.

From the above study, it has been deduced that HER dissolution is a solvation reaction rather than chemical dissolution and the H-bonding is responsible for it.

5. Delamination of large size WPCBs and post-treatment leaching of copper

Attempts to delaminate larger size WPCBs were also made by using DMA and results showed that with an increase in size, the time taken for delamination increases too much.

Post-treatment, WPCBs has been subjected to leaching in a hydrothermal bomb autoclave at 140 ^{o}C, 3M H_2SO_4, 90 min, 50 $g{\cdot}L^{-1}$ pulp density (optimized parameter chosen from M. Basha's M.Tech dissertation work) in presence of varying concentration oxidants like H_2O_2 and HNO_3. Results showed that using 15% H_2O_2 almost 96% Cu has been leached out, while only 5% HNO_3 leached 98% copper. Leaching of milled WPCBs of (-1 mm) showed that under similar conditions using 15% HNO_3 maximum 94% copper recovery is achievable. The SEM-EDS and XRD study also used to validate the leaching results.

These results show that organic solvent treatment is more favourable in view of commercialization of this technique over conventional technique. The relative merits of proposed process are- low oxidant consumption, more copper leaching, lower economy due to the regeneration of solvent, negligible effluent generation, easy handling (large pieces rather than fine powder form), simpler operation, low initial investment, low wear and tear (no mechanical parts) and thus less contamination etc.

Chapter 4 embodies the major outcomes drawn from this research work. References cited in the presentation are also given at the end, besides the scope of further work.