Electronic waste recycling via cryo-milling and nanoparticle beneficiation

C.S. Tiwary[1,3,4,*], S. Kishore[1,4], R. Vasireddi[2], D.R. Mahapatra[2], P.M. Ajayan[3] and K. Chattopadhyay[1,*]

[1] Materials Engineering, Indian Institute of Science, Banaglore 560012, India
[2] Aerospace Engineering, Indian Institute of Science, Banaglore 560012, India
[3] Materials Science and Nano Engineering, Rice University, Houston, TX, USA

The existing methods for recycling electronic wastes such as the printed circuit boards (PCB), which contains a large number of components and elements, face significant challenges when considering environmentally benign and easily separable disposal targets. We report here a low-temperature ball milling method that breaks down PCBs all the way into nanoscale particles which further enables enhanced separation of its different base constituent materials that are the polymer, oxide, and metal. The recovered materials are easy to be beneficiated as the nanoscale particles produced from milling are mostly single phase particles, compared to the larger particles obtained by other methods that are multiphase mixtures of various constituents. In addition, the recovered nano size particles can be used as starting material for making useful products such as polymer nanocomposites. Our method demonstrates a new and simple nanoparticles beneficiation route for the processing and recycling of electronic wastes into fully separable constituents.

Introduction

The last decade has seen an exceptional increase in the technology and the use of electronic goods [1–3]. This growth has also led to the creation of immense amounts of e-waste. In 2013 alone nearly 50 million tons of e-waste was generated worldwide. United Nations' STEP initiative has reported that e-waste is expected to grow by 33% for next 4 years [4,5]. The projected data shows that by 2030 the obsolete computer waste will reach 1000 million tons. These electronics wastes often contain toxic substances. Nearly 80–85% of electronic products were directly disposed of in landfills or incinerators. E-waste represents 2% of America's trash in landfills, but it amounts to 70% of the overall toxic waste of the country [4–11]. According to the United Nations Environment Program annually about 50 million tons of e-waste is generated in the world. In the year 2011, 3410 kilotons of waste were generated in the USA [4]. On the other hand, the cumulative amount of the e-waste, which the USA has recycled, is only 12.5%. As per EPA report, e-waste continues to be the fastest growing municipal waste stream in America. Most of the electronic appliances turn into e-waste and a minuscule amount is recycled. These critical issues of e-waste are raised by several recent scientific and public reports, and it has attracted a lot of social and scientific attention [6–10] and beg for a sustainable solution. In order to handle the e-waste problem scientists and technologists have been working together for a long time [11–21]. Till date, to the best of our knowledge, there are only two major commercial methods of recycling PCBs which are reported in published literature [11–21]. One of them is physical methods involving incineration and crushing which is one of the oldest methods and used in several underdeveloped countries [11–21]. In this method, organic polymers are removed by incineration followed by crushing that leaves out metals and ceramics for further recovery and beneficiation. Incineration is a method which helps in extraction of metal and alloy components (although mixed) and does not offer the

*Corresponding authors:. Tiwary, C.S. (cst.iisc@gmail.com), Chattopadhyay, K. (kamanio@materials.iisc.ernet.in)
[4] These authors contributed equally to this work.

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possibility to reuse polymers. It also causes emission of dioxins and furans which possess a serious threat. The second and a more recent method is a chemical method involving mechanical treatment followed by pyrolysis or hydrometallurgy of the PCB and other e-wastes [11–21]. Here, a PCB is crushed into centimeter-sized particles. The large particles are then treated with heat and chemicals to separate and extract materials. In this process, most of the recovered materials have multiple components (due to the large particle sizes of broken down wastes) making it very difficult to extract pure phases which could be of direct use. Overall, the separation of metals, ceramic (oxides) and polymers present in e-wastes (as shown in Fig. 1a and b) in a cost-effective and environment-friendly manner remains a significant challenge. In this paper, we propose a new approach to address the above challenge using nanoscale processing. The approach hinges on the idea of breaking down the waste into nano-size powders which essentially become single phase particles, which can be easily separated.

An optical mouse was used for demonstrating the material recovery. The optical mouse was dismantled and Printed circuit board (PCB) was removed from it. The PCBs were of 2.6206 g weight. The two PCB's were milled for 30 min using a specially designed cryo-mill. A temperature of 154 K was maintained during the entire milling time. The in-house designed cryomill can mill using single hardened steel ball in an inert atmosphere maintain using a flow of Argon. The temperature of the container is maintained using a continuous flow of liquid nitrogen (Fig. 2b). A detailed description about the mill is described in our previous work [22–26]. FEG-EPMA was used for element identification in the cryo milled PCB powder. The phases were analyzed using X-ray diffraction (X-Pert Pro, Pan Analytical). The sample was then subjected to particle size analyzer and TEM (transmission electron microscopy) (FEI, FEG TECHNAI F30) for the identification of nanoparticles. The size analyses of the suspended particles were carried out using a Zeta Sizer with a resolving capability by 0.3 nm. The same observation is performed using larger PCB board of computer mouse as shown in supplementary figures (Figs. S1 and S2). Commercially available epoxy phenol novolac resin, Araldite LY 5052 (Huntsman Advanced Materials, India) has been used as the matrix for the nanoparticle reinforcement. Aradur 5052 CH (India) was used as curing agent for Araldite LY 5052. The solution was stirred using the shear mixer at 20 rpm for 20 min then the mixture was allowed to cool down for 10 min. Hardener (38% by weight of epoxy) was then added to cure the resin. The obtained mixtures were poured into cylinder shaped plastic molds having dimensions of 12 mm $\times$ 6 mm and were allowed to cure at room temperature for 24 hours then cure at 50 $^{\circ}$C for 15 hours and followed by vacuum desiccation for 24 hours. The compression strength of the composites was determined using Universal Testing Machine (UTM, MAKRON). All the compression tests were carried out in accordance with ASTM 695 and the specimen dimensions were kept as 12 mm $\times$ 6 mm for the test. For all the specimens, the edge parallelism was ensured using polishing within 2 μm to avoid generation of stresses at the sample edges due to uneven distribution of load.

The PCBs (the e-wastes we primarily use here, but should be applicable to other e-wastes as well) are crushed in a specially designed cryo mill (KC-0, developed by the author's group at IISc Bangalore, and licensed to Tau Instruments, India) which keeps the material at low temperature constantly during crushing [22]. This cryo-milling process is able to reduce the different classes of materials (metal, oxide, and polymer) to nanoscale powders in an about 1–3 hours [23–26]. In addition, the low-temperature processing eliminates hazardous reaction and emission [24]. The resulting nanoscale powders are then used directly to extract materials without using any additional chemical methods. Fig. 2 shows the proposed protocol for recycling PCBs. For demonstration, we used PCBs taken from computer mouse as shown in Fig. 2a. A 30 min milling and a temperature of 154 K is maintained during the entire duration of milling with the help of continuous liquid nitrogen flow (Fig. 2b). In order to understand the mechanism of breakdown of materials during milling, we have collected samples in between, as shown in Fig. 2c and d. Fine powders produced as a result of 30 min milling are shown in Fig. 2e. The low and high magnification SEM images show nanoparticles in the form of 5–10 μm particles agglomerated (Fig. 2f and g). The X-ray diffraction (XRD) data of the milled powder confirms the presence of ceramic, polymer, glass and metal, as shown in Fig. 2h. The sizes calculated using FWHM (full width at half maximum) of the different peaks show a range of particle sizes of 20–150 nm. The particle size of powders measured using laser particle analyzer shows bimodal distribution (with a mean size of <50 nm and 200 nm) as shown in Fig. 2i. The XRD analysis reveals that the crystalline powders belongs to metal (Cu, Ag, Au, Al, Pb, Sn, etc.) and alloys of Fe–Si, Cu–Ti, etc. The oxide presents are predominantly complex oxides of Ca, Mg, Si, Pb, Ti oxide. In the current study, we show two methods for recycling the e-waste, the first via nanoparticle beneficiation or separation into the individual classes of materials (metals, oxide and polymers; Fig. 2e) and a second via the consolidation of milled and partially separated, predominantly polymer constituents, into polymer composites that can be directly used as mechanical structures (Fig. 2e).

We first discuss the beneficiation route via the separation of cryo-milled fine e-waste powder. When the powder is mixed with water it forms two clearly separable layers; one is a floating layer and the other sediment layer as shown in Fig. 3a. Both these layers are separated (as shown in Fig. 3b and e) and further analyzed. The top layer is diluted further, which gives rise to a colloid as shown Fig. 3b. The particle size distribution is obtained using the TEM images shown in Fig. 3d. This distribution confirms the presence of nanoparticles with a mean size range of $\sim$20 nm (Fig. 3d). These polymer-based colloids of nanoparticles are shown in Fig. 3c. These polymer nanoparticles can be used further in 3D printing, polymer powder based paint and as reinforcement in a composite. The second layer of sediment collected at the bottom is further separated by dilution in water and shaking for (as shown in Fig. 3e). The top part out of this is collected and its composition analysis shows Mg, Si, Pb, Sn, Cu, Co and Ca oxides (Fig. 3f). The bright field images of the Ca and Si oxide nanoparticles (size less than 100 nm) are shown in Fig. 3g and h respectively. The part settled at the bottom is separated further, first using a magnet as shown in Fig. 3k. This removes magnetic particles (mostly Fe/Co-based, see Fig. 3k). Analysis of the composition of the bottom layer shows an absence of polymer or oxide (using FEG-EMPA). This layer contains nanoparticles of Ag, Au, Sn/Pb, Cu, Al, Ni, and Cu (as shown Fig. 3i–o) as analyzed using TEM bright field imaging and EDS. The size and compositions are measured with the help of

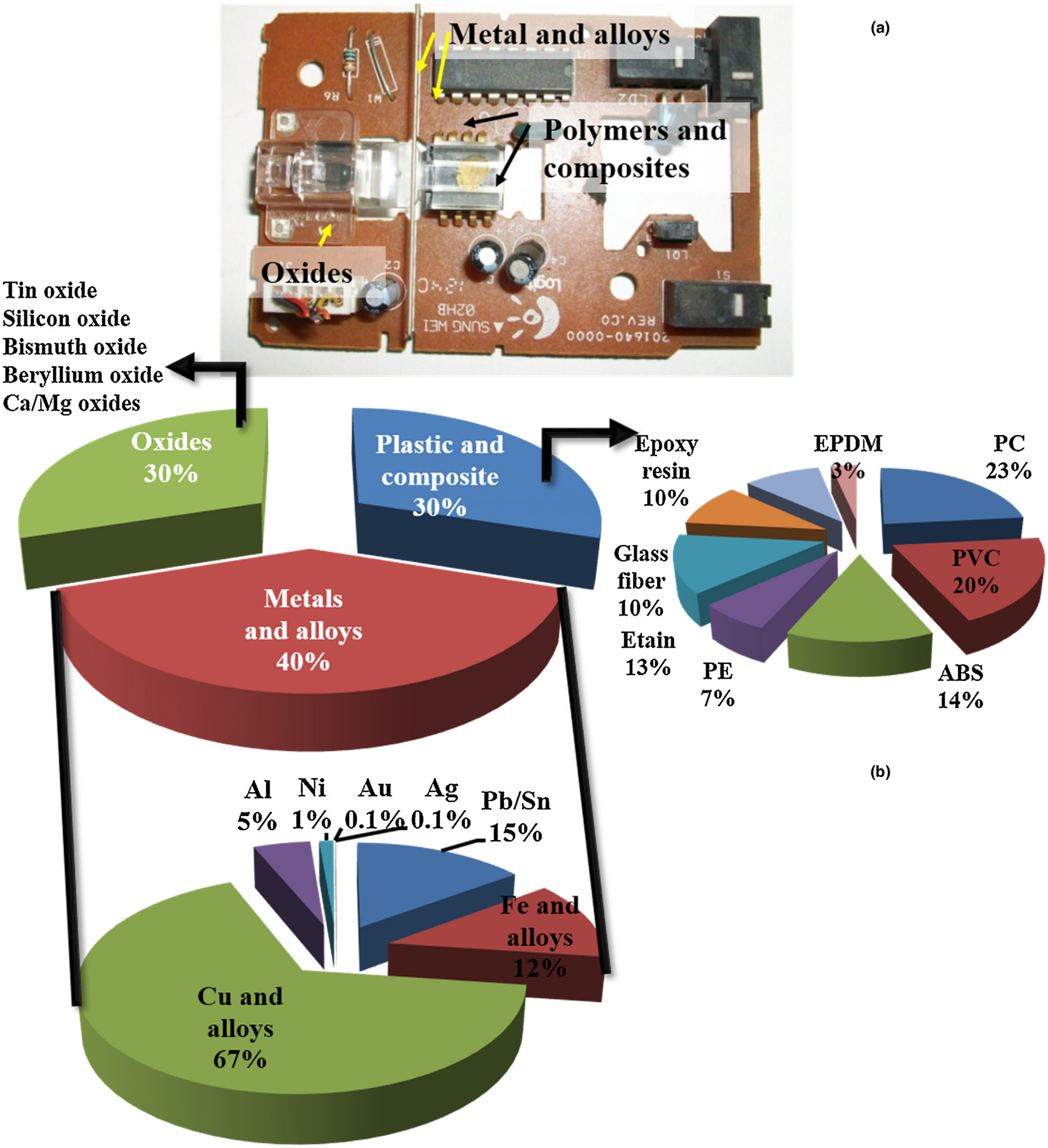

FIGURE 1

(a) An example of PCB board from the optical mouse, marking the presence of the different class of materials (metals, oxides, and polymers) used in the board, depicting the complexity of the materials problem. (b) A pie diagram of the fraction of constituent materials presents in a representative PCB board. The three classes of materials (metal and alloys, oxides and polymer and composites) present are further divided in the subclass as shown in other pie charts (data is summarized from [11–21]).

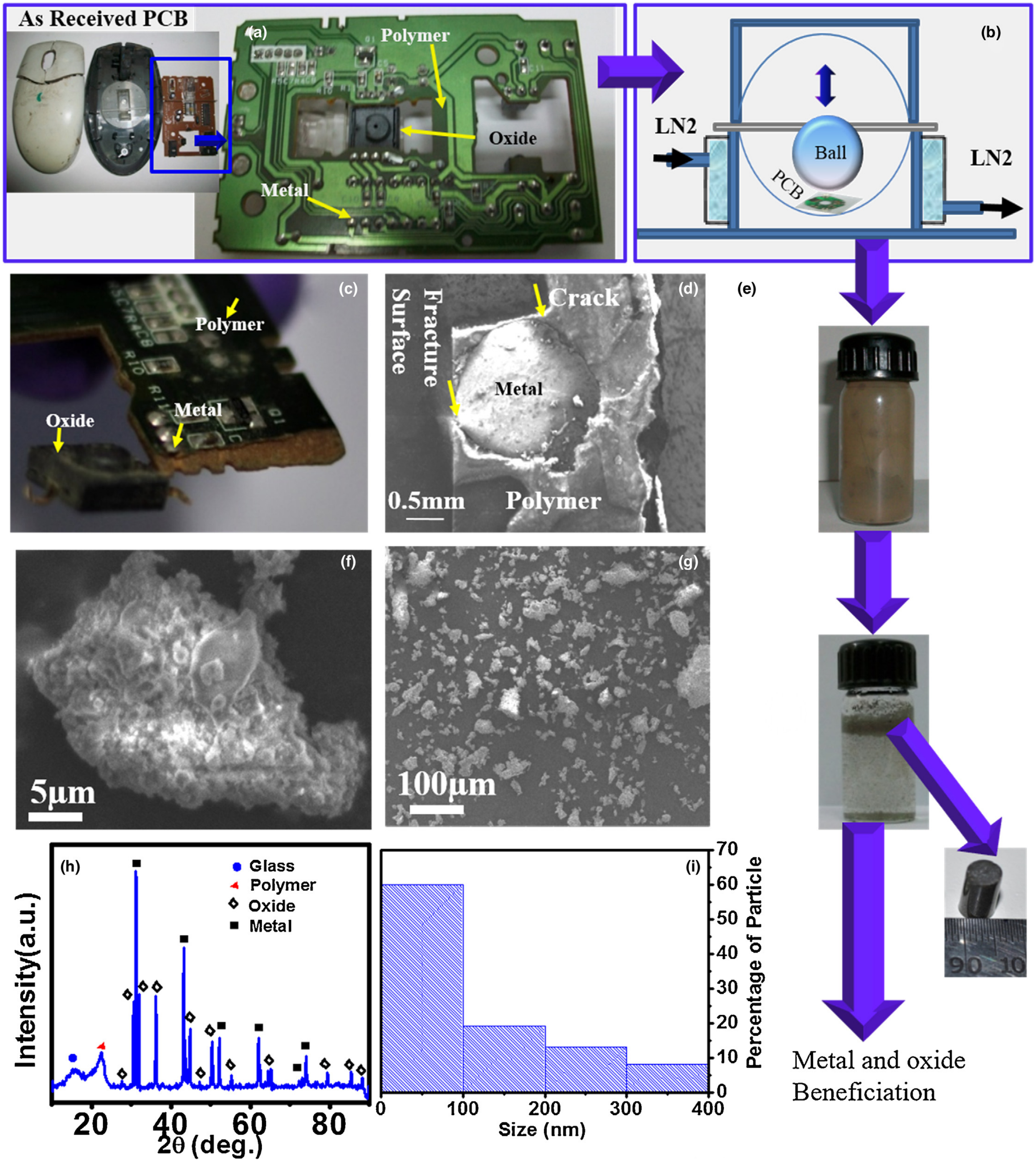

FIGURE 2

Flow layout for the simplified recycling method proposed in current work. (a) The digital image of computer mouse PCB used in current work. (b) Schematic image of the cryo mill (KC0) used for crushing the PCBs (Single ball containing vibratory mill with inert atmosphere. The sample container is cooled using liquid nitrogen.). (c) Digital and (d) the SEM image of the sample after 2 min showing initial separation of the component of PCB (e) The collected powder of PCB board after the 30 min milling. The powder is used in two different processing one for recovery of metals and other for making a polymer composite. (f) and (g) SEM image of the powder at two different magnifications. (h) XRD plot of the PCB milled for 30 min in the Cryo-mill. (i) Particle Size distribution using laser particle analyzer of the cryo-milled PCB board.

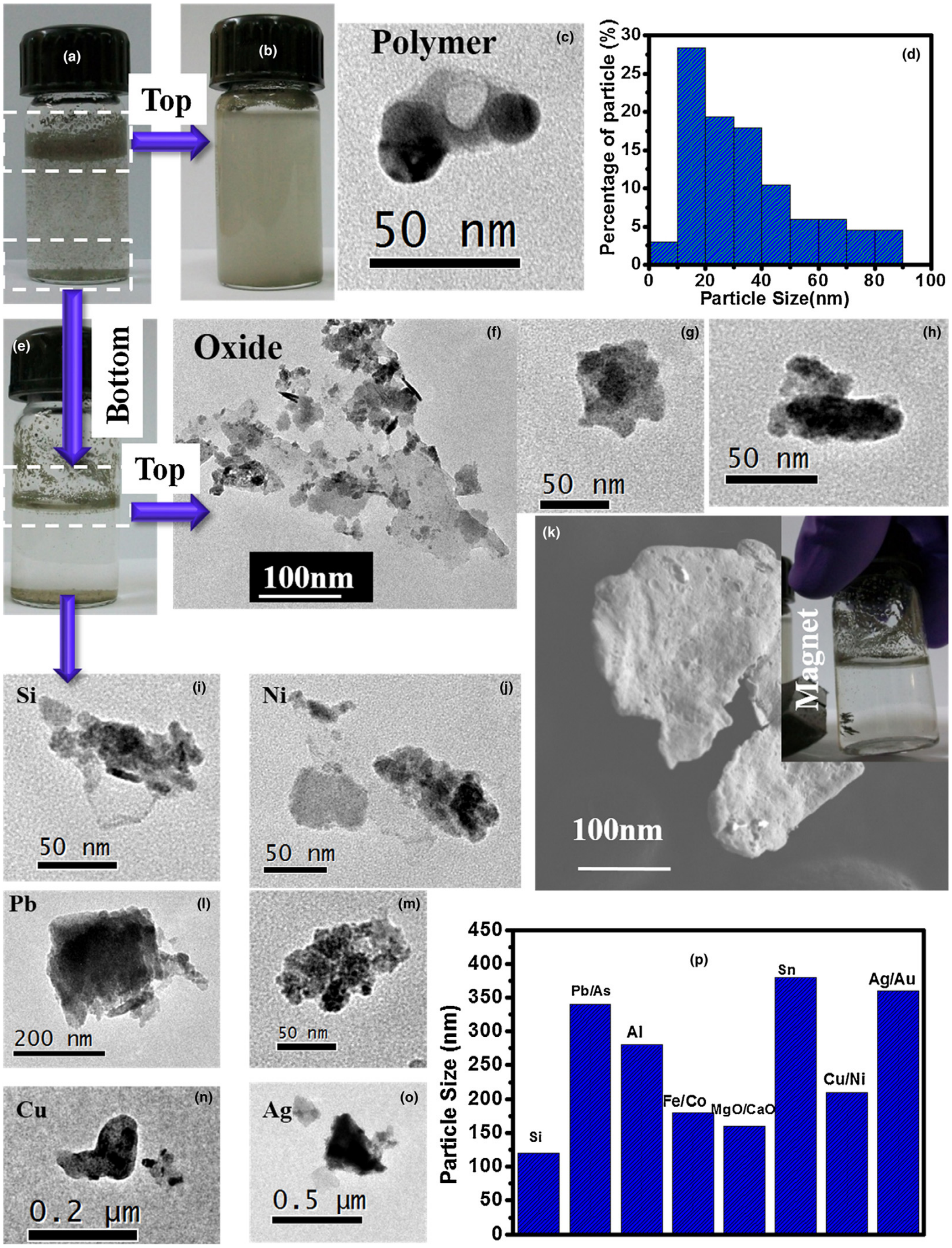

FIGURE 3

(a) Digital image of the powder produced in milling and dissolved in water. Separation of the powders due to different densities when mixed with distilled water. The two top and bottom part of the powder in water. (b) The top part forms Colloid after mixing with distilled water and sonication for 5 min. (c) Bright field TEM images of the colloid particle. (d) Particles distribution of the colloids measured using several TEM images. (e) The powder collected from the bottom of the water is further dissolved in water showing two separate layers. (f) Low magnification image of top oxide layer (g) and (h) high magnification of image of two individual oxide particles of lead oxide and silicon oxide. (i), (j), (l)–(o) Bright field TEM image of individual metallic particles collected from bottom layer of the solution. (k) Separation of magnetic particles with the help of a magnet. (p) The mean particle size of different metals and oxide with the help of EDS attached to TEM.

TEM and EDS and are shown in Fig. 3p. It clearly shows that most of metal and oxide particles are in the range of 100–350 nm size. The beneficiation of these separated metallic nanoparticles can be further purified using several methods discussed in the recent report by Barbara et al. [27]. In the second approach, we demonstrate the use of e-waste powders as reinforcement in polymer composites. An example is demonstrated for epoxy based composites in supplementary Fig. S2. The mechanical properties of this composite are compared with a solid made of pure epoxy. The SEM of the e-waste added polymer reveals uniform dispersion of the nano-sized particles in the epoxy (supplementary Fig. S2). It reveals strengthening of the polymer due to the presence of nanoparticles of e-waste. This approach avoids any kind of disposal or any other chemical recovery effort and the composite formed could be utilized directly in mechanical applications (e.g. packaging).

The above results explain two interesting aspects. First, the reduction of different materials (polymers, metals, and oxides) into different sizes and second, the easy separation of the nanoparticles produced using sedimentation in water. The reduction of size in cryo-milling, all the way to the nano size, involves rapid fracturing as has been discussed in previous reports [22–26]. The three classes of materials (polymer, oxide, and metal) present in the PCBs have very different strengths and fracture toughness as shown in Fig. S4a and b (supplementary figure) [28]. It shows that oxide and metal have higher stiffness and strength in comparison to polymers, and hence on the application of the same load, the oxides and metals will, in general, deform less compared to the polymer. The fracture strain in the polymer is often higher at room temperature. However, the mechanical properties of the polymer vary as the temperature decrease (Fig. S4c) [28]. As a result, the polymer components fracture rapidly and forms smaller particles, at low temperatures. Metals and oxides have a similar range of fracture toughness and strength; hence, their characteristic sizes are very similar. In the case of PCBs, the interface of polymer, metal and oxide are strong and hence the separation becomes difficult at room/high temperatures. Milling at liquid nitrogen temperature, therefore, has an advantage in such type of processing. The large differences in the values of the coefficient of thermal expansion and thermal conductivity lead to a mismatch between the thin metal/oxide coating and polymer substrate at the interface leading to void formation and fracture initiation. As a result, they get easily separated under loading. The low-temperature processes lead to a highly efficient separation nanoparticles of metal, oxide, and polymer and produce a high yield of single phase nanoparticles. We have examined samples at various stages of milling (2 min, 10 min, and 20 min) as shown in supplementary figure (Figs. 2c, d and S1). The 2 min milled PCB shows the macro-fracture and fragmentation at the interface of polymer, metal, and oxide (Fig. S1), as marked in the figure. The SEM image at the edge of fragmented sample reveals fracturing of the constituents separately (shown in the supplementary figure, Fig. S1). The SEM images of particles show cracks at the interface of metal–polymer and oxide–polymer particles giving rise to a separate metal agglomerates and polymer particles. The room temperature milling of large pieces' results in surface grinding whereas the small pieces give rise to agglomerated chunk.

Another interesting observation is the separation of polymers from oxides and metals in aqueous media. This can be explained with the help of a mass density map proposed by Ashby (Fig. S4a) [28]. The polymers have the lowest density as compared to that of metals and oxides and hence they generally float on top of the water. On the other hand, the metals and oxides of similar size have a very different density as shown in Fig. S4a. The terminal velocity of the particle at the nanoscale (due to high surface to volume ratio) drastically changes with a small change in the density of the particle. Hence, at the nanoscale, the particles with a small difference in their densities can be separated easily [29,30,15,31,32]. Thus, reducing the powder to nano size improves the efficiency of separation of the particles having different densities [29,30,15,31,32]. The settled nanoparticles of metals can be recovered using conventional separation methods using mechanical (wet shaking table, eddy current separation, sedimentation in heavy medium, kinetic gravity separation, etc.) and magnetic separation.

Finally, the current method of separation of individual particles from complex, heterogeneous and composite structure of PCB

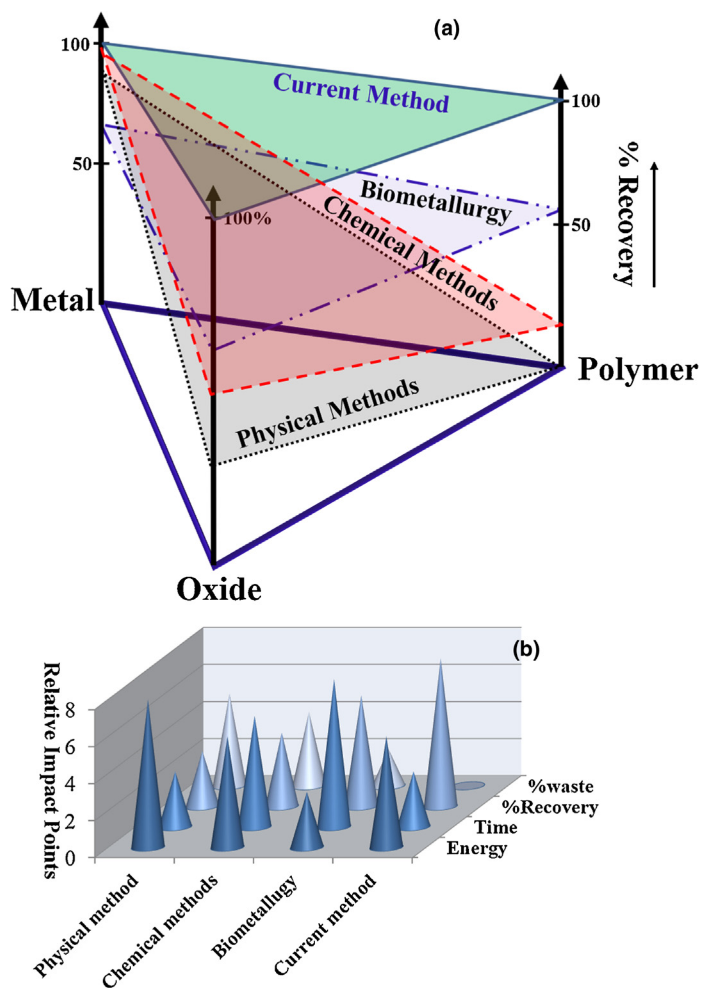

FIGURE 4

(a) A qualitative representation of percentage of recovery plot of ternary system (metals, oxide and polymer) in different methods (physical methods (crushing and heating to high temperature), chemical methods (crushing followed by Pyrometallurgy and hydrometallurgy, etc.) and Biometallurgy (beneficiation using biological entities)) and its comparison with current proposed method. (b) A relative comparison of these methods in terms of energy consumption, time for the process, percentage recovery of all the materials and the total waste generated during the process.

boards is compared with existing beneficiation [11–21] techniques as shown in Fig. 4a and b. The physical methods consist of crushing the PCB into cm size pieces and heating to the high temperature (>500 °C) and subsequently extracting metals, losses polymer and oxide (Fig. 4a) [12–16]. Such methods take a large amount of energy and give rise to a large amount of waste in the form of gas and slag during heating (Fig. 4b). The chemical methods, mostly involving Pyrometallurgy and hydrometallurgy, are able to extract the metal and oxide components at higher yields as compared to physical methods as shown in Fig. 4a [11–21]. It involves lower energy but takes longer time and gives rise to the high fraction of chemical waste compared to physical methods (Fig. 4a and b). Recently developed eco-friendly methods such as Biometallurgy recover all three fractions in moderate fractions [17]. It involves lower energy consumption but needs longer time and hence rate of recovery is low as compared to previous two. In our current proposed method, the low-temperature milling to nanoparticles fully separates the components into single phase particles, which can be easily separated and recycled as pure components, which none of the above methods are able to achieve. The ability to separate into individual components could provide this method a better cost advantage since many of the species that are separated could be recycled and used directly in the high-value chain applications, for example as pure metals. The method is also scalable and environmentally friendly since the main process is done at low temperature. Although the approach needs higher energy compared to chemical and biometallurgical methods, it allows for the best recovery and limited waste. The new approach can be developed into an eco-friendly method to address the imminent serious problem of e-waste management. The efficiency of the current method of cryo milling using liquid nitrogen cooling can be further improved with help of closed cycle. The current milling can be easily scaled up with help of recent development of pneumatic grinding.

Author's contributions

C.S.T. generated idea and designed the experiments with SK, RV and DRM. DRM, KC, CST and PMA guided the project and wrote the manuscript. All authors contributed to the overall scientific interpretation and edited the manuscript.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.mattod.2017.01.015.

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