Review

Recycling of non-metallic fractions from waste printed circuit boards: A review

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ABSTRACT

The major economic driving force for recycling of waste printed circuit boards (PCBs) is the value of the metallic fractions (MFs) of PCBs. The non-metallic fractions (NMFs), which take up almost 70 wt% of waste PCBs, were treated by combustion or land filling in the past. However, combustion of the NMFs will cause the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) while land filling of the NMFs will lead to secondary pollution caused by heavy metals and brominated flame retardants (BFRs) leaching to the groundwater. Therefore, recycling of the NMFs from waste PCBs is drawing more and more attention from the public and the governments. Currently, how to recycle the NMFs environmental soundly has become a significant topic in recycling of waste PCBs. In order to fulfill the better resource utilization of the NMFs, the compositions and characteristics of the NMFs, methods and outcomes of recycling the NMFs from waste PCBs and analysis and treatment for the hazardous substances contained in the NMFs were reviewed in this paper. Thermosetting resin matrix composites, thermoplastic matrix composites, concrete and viscoelastic materials are main applications for physical recycling of the NMFs. Chemical recycling methods consisting of pyrolysis, gasification, supercritical fluids depolymerization and hydrogenolytic degradation can be used to convert the NMFs to chemical feedstocks and fuels. The toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) can be used to determine the toxicity characteristic (TC) of the NMFs and to evaluate the environmental safety of products made from the recycled NMFs. It is believed that physical recycling of the NMFs has been a promising recycling method. Much more work should be done to develop comprehensive and industrialized usage of the NMFs recycled by physical methods. Chemical recycling methods have the advantages in eliminating hazardous substances in the NMFs. The trend in chemical recycling of the NMFs is to make the best of advantages over physical recycling of the NMFs to compensate its higher cost. Removing and treating the hazardous substances in the NMFs is an ultimate method to eliminate the pollution.

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Contents

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1. Introduction

The production of electrical and electronic equipment (EEE) is one of the fastest-growing sectors of the manufacturing industry in the world. At the same time, technological innovation and intense marketing engender a rapid replacement process. Every year, 20–50 million tonnes of waste electrical and electronic equipment (WEEE) are generated worldwide, which could bring serious risks to the human health and the environment [1]. It is not only a crisis of quantity but also a crisis arising from toxic ingredients, such as the lead, beryllium, mercury, cadmium, and brominated flame retardants (BFRs) that pose both occupational and environmental health threats [2]. The printed circuit boards (PCBs) are the platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. PCBs provide the electrical interconnections between components and are found in virtually all EEE. The production of PCBs is the basis of the electronic industry as it is an essential part of almost all EEE. The PCBs are crucial to the manufacture and sales of about $1 trillion of EEE each year [3]. In recent years, the average rate of worldwide PCBs manufacture increased by 8.7%, and this figure is much higher in Southeast Asia (10.8%) and Mainland China (14.4%). As one of the most important branches of WEEE stream, waste PCBs (seen in Fig. 1) have drawn more and more attention of the public and researchers because plenty of toxic materials including heavy metal and BFRs can be easily found in them and they cause huge damage to the environment [4–6] if they are not recycled properly (seen in Figs. 2–4).

PCBs are a mixture of woven glass fiber or cellulose paper reinforced resin and multiple kinds of metal. Their special physical and chemical characteristics make them difficult to recycle them. However, recycling of waste PCBs is an important subject not only for the protection of environment but also for the recovery of valuable materials. In general, the components of waste PCBs can be divided into metallic fractions (MFs) and non-metallic fractions (NMFs). Non-metallic fractions are called non-metals, non-metallic materials, glass fiber–resin powder (GR powder), glass–non-metals, epoxy resin compounds or other names by different researchers. In this review, all of those versions are collectively called non-metallic fractions and are abbreviated as NMFs. Currently, recycling of waste

Fig. 2. Open burning of wires and other parts to recover metals such as steel and copper is commonplace [2].

PCBs can be broadly divided into three major stages:

- Pretreatment and disassembly: Hazardous or reusable components are pretreated and selectively disassembled;
- Size reduction and separation: The size of waste PCBs is reduced to proper value and the MFs and the NMFs are separated by using mechanical processing or chemical processing;
- Recycling: The MFs and the NMFs are recycled separately.

Much work has been carried out to investigate each stage of waste PCBs recycling [7–9] by different researchers, of which recycling of the NMFs is one of the most significant and difficult processes. The NMFs consist of thermosetting resins, reinforcing materials, BFRs and other additives and take up about 70% weight content of waste PCBs. Thermosetting resins cannot be remelted or reformed due to their network structure. The major economic

Fig. 1. Waste printed circuit boards (PCBs).

Fig. 3. Dump of acid-treated circuit boards and processing residues along the Lian-jiang River [2].

Fig. 4. Recovering gold from waste PCBs using acid baths [2].

Table 1
Typical composition of printed circuit boards (PCBs) [7].

Element	Ag	Al	As	Au	S
Content	3300 g/t	4.7%	<0.01%	80 g/t	0.10%
Element	Ba	Be	Bi	Br	C
Content	200 g/t	1.1 g/t	0.17%	0.54%	9.6%
Element	Cd	Cl	Cr	Cu	F
Content	0.015%	1.74%	0.05%	26.8%	0.094%
Element	Fe	Ga	Mn	Mo	Ni
Content	5.3%	35 g/t	0.47	0.003%	0.47%
Element	Zn	Sb	Se	SiO_2	Sn
Content	1.5%	0.06%	41 g/t	15%	1.0%
Element	Te	Ti	Sc	I	Hg
Content	1 g/t	3.4%	55 g/t	200 g/t	1 g/t
Element	Zr	Sr			
Content	30 g/t	10 g/t			

2. Compositions of waste PCBs and characteristics of the NMFs

2.1. Compositions of waste PCBs

The choice of manufacturing materials used for PCBs depends on the application, for example, difunctional epoxy resins are adequate for simple two-sided circuit boards but more sophisticated multifunctional epoxy resins or cyanate esters are required for thick multi-layered boards [27,28]. Two common type PCBs are made of glass fiber reinforced epoxy resin (referred to commercially as FR-4) or cellulose paper reinforced phenolic resin (FR-2). FR-4-type PCBs are used in high-value EEE and FR-2 types are used in televisions and home electronics [29]. PCBs contain significant quantities of metals such as copper, iron, nickel, silver, gold, and palladium. Other metals that are present in waste PCBs include the electrical components themselves and the solder used to attach them to the boards [30]. The Rönnskar smelt plant of Sweden analyzed the typical compositions (Table 1) of waste PCBs [31].

The components mounted on PCBs generally include chips, connectors, capacitors, etc. [32]. Different components have a different material composition [33,34]. Material composition of PCBs is, therefore, quite complex and causes problem for the recycling of waste PCBs. The materials present in PCBs can be categorized in three groups: organic, metals, and ceramics. In general, PCBs mounted with components consist of approximately 40% metals, 30% plastics, and 30% ceramics [7]. For waste PCBs without mounted electronic parts, the material composition is made up about 28 wt% metals (mainly copper) and 72 wt% non-metallic materials [35].

2.2. Characteristics of the NMFs

The NMFs consist of cured thermosetting resins, glass fiber (cellulose paper), ceramics, BFRs, residual metals and other additives. The material compositions vary with the source and type of waste PCBs and the separation processing. In a study carried out by Yokoyama and Iji [36], the NMFs consisted of glass fiber (65 wt%), cured epoxy resin (32 wt%), and impurities (copper: <3 wt%, solder: <0.1 wt%). The residual metal (mainly copper) in the NMFs, which were separated from waste PCBs without mounted electronic parts by using the CES, was characterized by Guo et al. [37] and the results

driving force for recycling of waste PCBs is the value of the MFs contained in PCBs. The NMFs were treated by combustion or land filling in the past. However, combustion of the NMFs will cause the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) while land filling of the NMFs will lead to secondary pollution caused by heavy metals and BFRs leaching to the groundwater. Therefore, the NMFs must be recycled in an environmentally sound way, which has become a great challenge faced by recycling of waste PCBs. At present, recycling of the NMFs from waste PCBs is drawing more and more attention from the public and the governments. In order to give a fundamental understanding of recycling of the NMFs from waste PCBs and provide a detailed research status for further investigation in this paper, the recycling methods and outcomes of the NMFs from waste PCBs and analysis and treatment for the hazardous substances contained in the NMFs are reviewed on the basis of our previous study.

In general, the recycling methods of the NMFs from waste PCBs can be summarized as physical recycling methods and chemical recycling methods. Physical recycling methods of the NMFs are adopted after the MFs and the NMFs have been separated from waste PCBs by using mechanical processing [10]. Mechanical processing for the separating the MFs and the NMFs from waste PCBs includes shape separation, magnetic separation, electric conductivity-based separation, density-based separation and corona electrostatic separation, all of which have been well reviewed by Cui [11] and Huang et al. [12]. Corona electrostatic separation (CES) for the MFs and the NMFs from waste PCBs has been intensively studied by Xu and his colleagues from Shanghai Jiao Tong University in China [13–24] and has been proved to be a highly efficient and environmental friendly process. Chemical recycling methods of the NMFs are adopted during and after the stage of the chemical separating process for the MFs and NMFs in chemical recycling methods for waste PCBs. Chemical recycling methods [25] include pyrolysis, gasification, depolymerization process using supercritical fluids and hydrogenolytic degradation. The environmental safety analysis and evaluation of the products made from the recycled NMFs from waste PCBs is also an important issue. The hazardous substances contained in the NMFs are mainly BFRs (tetrabrombisphenyl-A (TBBA), etc.) and residual heavy metals (lead, chromium, mercury, cadmium, etc.) [26]. The fate and substance flows of these hazardous substances are important during the recycling of the NMFs from waste PCBs. Removing and treating BFRs and heavy metals contained in the NMFs is an ultimate method to eliminate the pollution caused by the hazardous substances.

Table 2
Component of non-metallic fractions (NMFs) from waste PCBs [37].

Size range (mm)	wt%	wt% of Cu	vol% of Cu (volume fraction)
0.3–0.15	11.8	0.42	0.11
0.15–0.09	22.5	0.34	0.09
0.09–0.07	29.8	0.40	0.10
<0.07	35.9	7.05	1.76

Table 3
Material content of the NMFs recycled from waste PCBs [38].

Specimen	NMFs particle size	Cu content (wt%)	Glass fiber content (wt%)	Resin, etc. content (wt%)
1	Fine	1.64	71.50	26.86
2	Medium	1.05	55.50	43.45
3	Coarse	0.48	46.00	53.52

Table 4
Formulations of PMC [40].

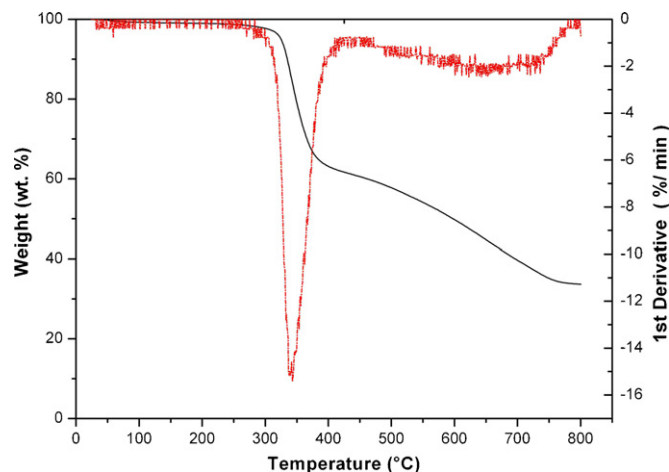| Ingredients	Content (wt%) of reference PMC	Content (wt%) of modified PMC
Phenolic resin	43	40–47
Wood flour	34	5–25
Nonmetals	11.6	10–40
Talc powder	7	3–15
Hexamethylenetetramine	0.6	7
Calcium carbonate	0.6	0.6
Magnesium oxide	1.6	0.6
Nigrosine	1.6	1.6
Stearic acid	43	1.6

Fig. 5. TGA diagram for non-metallic fractions (NMFs) separated from FR-4 type PCBs without mounted electronic parts by using the CES measured in a nitrogen flow of 50 ml/min at a 20 °C/min heating rate (initial mass 4.9440994 mg).

enough for physical recycling methods for the NMFs. As for chemical recycling methods, the degradation temperature (below 471 °C) is reasonable.

3. Physical recycling of non-metallic fractions from waste PCBs

According to their applications and properties, synthetic polymers can be classified as plastic, rubber, fiber, adhesive, etc. Plastics include thermoplastic plastics and thermoset plastics. Plastics consist of resin, filler and addition agents. In general, the fillers for polymers have two functions: one is to reduce the cost of the products, and the other one is to enhance the performance of the products. Sometimes the properties of filler are crucial to the performance of polymer products, especially for composites. The invention of glass fiber reinforced composites has great effluence on space aeronautical industry and other industries. Nowadays, superior performance fillers play a key role in high-tech material areas. Therefore, how to take advantage of filler for polymer products is a significant topic. The thermosetting resins, glass fiber (cellulose paper), ceramics and residual metals contained in the NMFs from waste PCBs can serve as good filler for different resin matrix composites. In fact, most researchers recycle the NMFs as fillers for thermosetting resin composites and thermoplastic resin composites when considering physical recycling methods.

Concrete is a versatile and most popular construction material. To be used as a raw material for concrete is also considered as a promising application for the NMFs. Over recent years, an appreciable number of structures around the world have been strengthened using fiber reinforced polymer materials, and the rate at which the technique is being used is increasing rapidly [39]. The addition of the NMFs to concrete can enhance the engineering properties of concrete such as strength, durability, shrinkage and permeability.

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscoelasticity is the result of the diffusion of atoms or molecules inside of an amorphous material. Viscoelastic materials include amorphous polymers, semicrystalline polymers, asphalt materials, etc. The glass fibers and resins contained in the NMFs can enhance

are shown in Table 2. In another paper [38], in which air classification was used as a separation process, residual copper, glass fiber and resin, etc. contents (Table 3) were different with the former two studies. When chemical methods are chosen to separate the MFs and NMFs, the cured thermosetting resins and the BFRs in the NMFs are transformed to micromolecules and therefore the final composition of the NMFs can be much more complex, which are discussed in a later section of this paper.

The thermal stability of the NMFs is very important both for physical recycling methods and chemical recycling methods. But the demands for the thermal stability in the two methods are just the opposite. In physical recycling methods, the NMFs have to be thermal stable in the injection molding or compression molding. For chemical recycling methods, the energy cost will be uneconomical if the degradation temperature of the cured thermosetting resins in the NMFs is too high. The TGA diagram of the NMFs separated from the most common FR-4 type PCBs without mounted electronic parts by using the CES is shown in Fig. 5. From Fig. 5, it can be seen that the degradation rate was greatest when the temperature was 343 °C and the onset temperature was 323 °C. When the temperature was 471 °C, the corresponding weight was 59.4% and most of the resins had decomposed. The residual weight was 33.4% at 800 °C. Because the upper temperature in most molding processes is below 323 °C, the thermal stability of the NMFs is good

Recycled nonmetals → Molding powders → Molding products
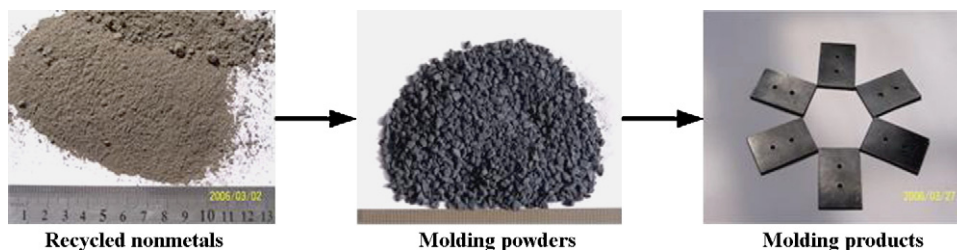
Fig. 6. The specimens of PMC [41].

Table 5
Effects of content of the NMFs on properties of PMC [40].

Properties	Standard	0	10%	20%	30%	40%
Relative density	≤1.45	1.40	1.40	1.39	1.39	1.38
Impact strength (notched)/(kJ/m^2)	≥1.5	2.1	2.4	2.3	2.4	2.7
Heat deflection temperature (°C)	≥140	154	157	168	164	169
Flexural strength (MPa)	≥70	71	64	70	70	71
Dielectric strength (90 °C) (mV/m)	≥3.5	3.9	3.3	3.9	3.9	5.0
Rasching fluidity (mm)	≥100	135	132	103	75	62

Table 6
Effects of particle size of the NMFs on properties of PMC [40].

Properties	Standard	Ref. PMC	0.3–0.15 mm	0.15–0.07 mm	<0.07 mm
Relative density	≤1.45	1.40	1.39	1.39	1.39
Impact strength (notched)/(kJ/m^2)	≥1.5	2.1	2.4	2.2	2.0
Heat deflection temperature (°C)	≥140	154	162	157	150
Flexural strength (MPa)	≥70	71	64	60	86
Dielectric strength (90 °C) (mV/m)	≥3.5	3.9	3.6	3.0	4.5

viscoelastic materials by composition effect to improve the temperature susceptibility.

3.1. Recycling the NMFs from waste PCBs as a filler for thermosetting resin matrix composites

Phenolic resin is one of the most common and oldest thermosetting resins. Phenolic molding compound (PMC) is produced with phenolic resin, acting as a bonding agent, various fillers, solidifiers, and colorants under high temperature and a certain pressure. Because of their relative cheapness, ease of fabrication, high mechanical strength, heat resistance, and high dielectric strength, PMC is widely used and is in demand for radios, kitchen utensils, and electronic switches. Increasing production of PMC in recent years has greatly increased the need of wood flour, which is used as organic filler in the molding compounds. With the timber resource depletion and the increasing price of wood flour, it is an urgent assignment for producers of PMC to protect timber resources and reduce the cost of raw materials by finding alternative materials for wood flour. The NMFs from paper-based waste PCBs was used to replace wood flour for producing modified PMC by Guo et al. [40]. The waste PCBs were first pulverized in a process consisting of a coarse-crushing step and a fine-pulverizing step, using a shearing machine and a hammer grinder. Then, an electrostatic separator was used to separate the metals from the non-metals. After they were separated, the NMFs were screened by a vibrat-
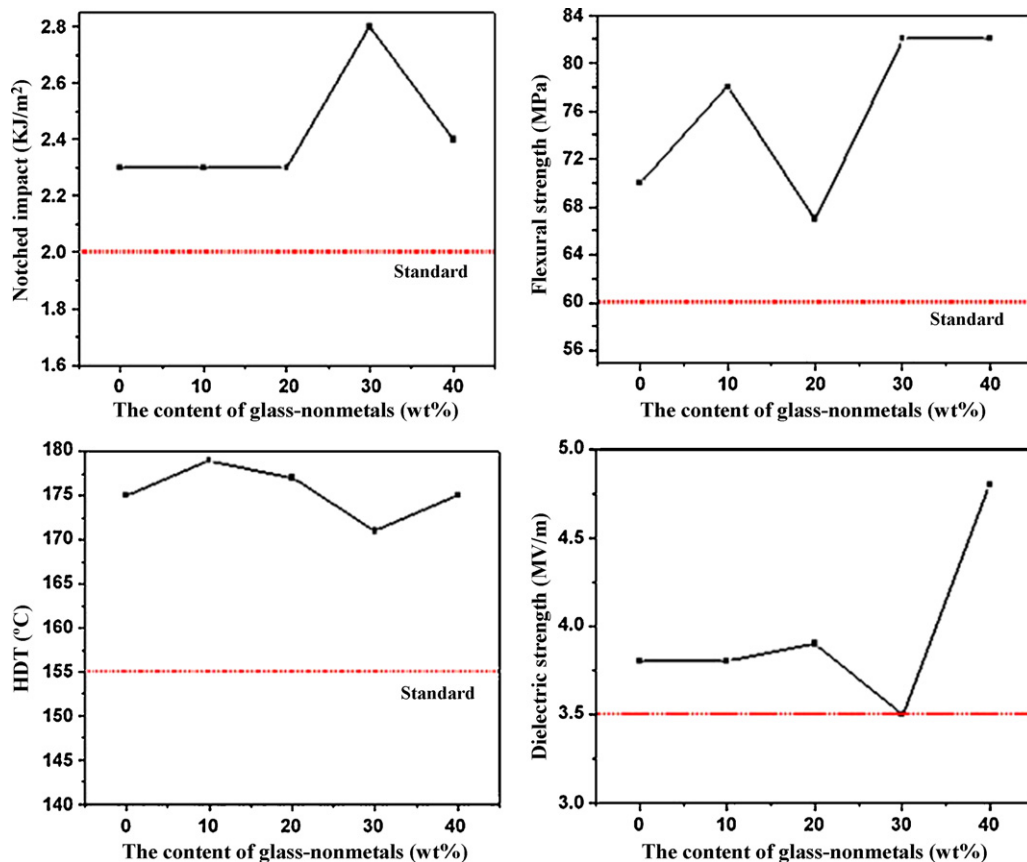

Fig. 7. Comparison of properties between reference PMC (RP) and PMC with glass-non-metals (PMCGN) [41].
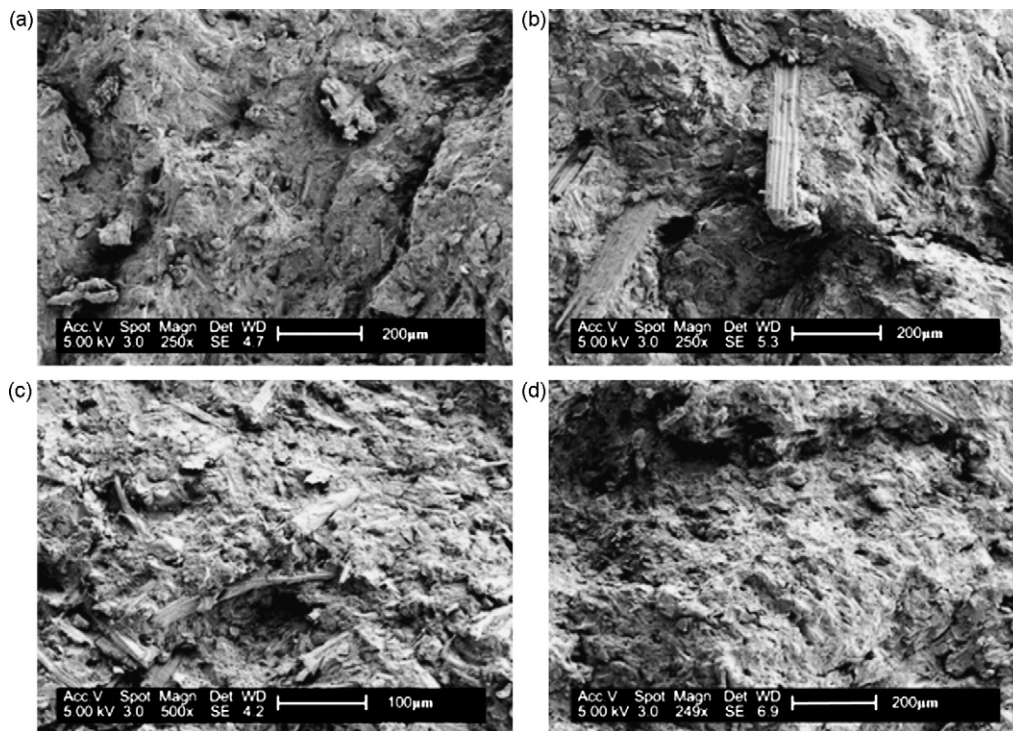
Fig. 8. SEM photographs of specimens filled with non-metals after flexural fracture: (a) ref, (b) 0.3–0.15 mm, (c) 0.15−0.07, and (d) <0.07 mm [40].

ing screen. Reference and modified PMC were prepared according to the formulations mentioned in Table 4. Properties of PMC with similar relative density can be compared. Thus, to maintain similar relative density, the proportions of wood flour and talc powder were adjusted. Phenolic resin was obtained as commercial grade from the Shanghai Twin-Tree Plastics Factory. The NMFs of PCBs were added to the raw materials mixture at weight fractions of 0, 10, 20, 30, and 40%. To ensure the surface smoothness, the size of NMFs used to study effects of different contents on the properties of PMC was less than 0.15 mm. The ingredients were premixed for 30 min in a blender to improve the dispersion of the components in the raw materials, and then the mixture of the resin, the fillers, and other constituents was mixed on a single-shaft, oscillating screw kneader at 95–105 °C. Then the melt was extruded by a two-roll press, cooled, and ground to a particle size of approximately 3 mm. Finally, these powders were compression-molded

into testing samples using different molds, according to the corresponding standards. The specimens of PMC are shown in Fig. 6. Properties of PMC filled with the NMFs are shown in Tables 5 and 6 and Fig. 7.

From the industrial application viewpoint, a recycling ratio (the amount of NMFs in the PMC) of 20% was most reasonable, which resulted in a flexural strength of 70 MPa, a charpy notched impact strength of 2.4 kJ/m^2, a HDT of 168 °C, a dielectric strength of 3.9 MV/m, and a rasching fluidity of 103 mm. The SEM photographs of reference and modified composites at three different particle sizes are shown in Fig. 8. The results indicate that making PMC with non-metals of waste PCBs provide a feasible method for resource utilization of the NMFs from waste PCBs.

Unsaturated polyester resins (UPRs) are one of the most widely used thermosets. UPRs find use in industrial applications because of their good mechanical properties especially when reinforced with
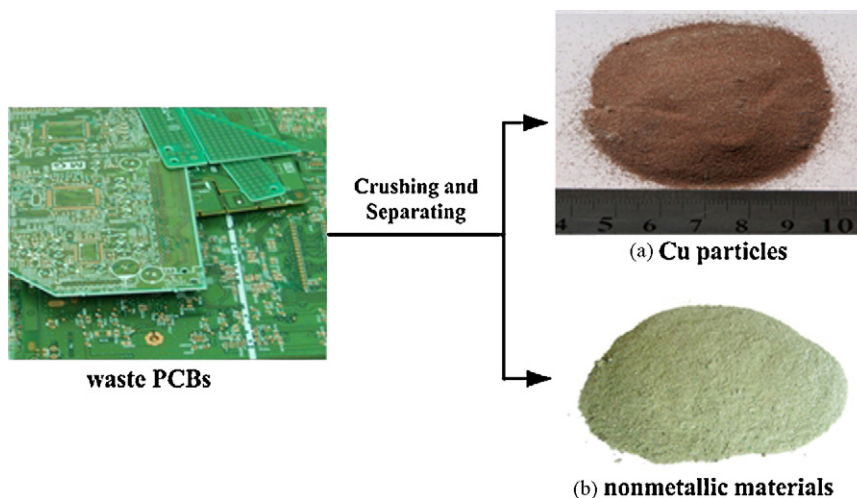

Fig. 9. Metallic fractions (MFs) (a) and the NMFs (b) of pulverized waste PCBs [37].

Table 7
Raw materials of the NMP [37].

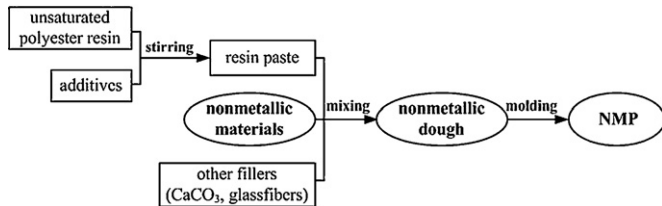| Ingredients	Content (wt%)
NMFs	0, 10, 20, 30, 40
CaCO3	64, 54, 44, 34, 24
Unsaturated polyester	18
Polystyrene	6
TBPB	0.2
Glass fiber	10
Zinc stearate	1

Fig. 10. Flowchart of preparation of the NMP [37].

fibers or fillers [42]. In order to take full advantage of the NMFs of waste PCBs, Zhenming Xu and his colleagues Jie Guo, Bin Cao, Jiuyong Guo from Shanghai Jiao Tong University have developed a novel technique to produce the non-metallic plate (NMP) by using unsaturated polyester resin as a bonding agent [37,43]. The waste PCBs used in their study are a kind of woven glass fabric copper clad laminate without electronic elements, so the NMFs only consists of Cu. The Cu particles and non-metallic materials after two-step crushing and electrostatic separating are shown in Fig. 9. Then, NMFs was screened and ground into four size ranges: 0.3 to 0.15, 0.15 to 0.09, 0.09 to 0.07, and <0.07 mm. Table 7 shows the raw materials of the NMP. The content of NMFs of waste PCBs and CaCO$_3$ was kept at a constant value of 64 wt%. The NMFs was added to the raw materials mixture at weight fractions of 0, 10, 20, 30, and 40%. Unsaturated polyester (UP) was used as a bonding agent due to its low viscosity, fast cure, excellent chemical resistance, and low cost. When UP was used, other additives were needed to complete the curing process of UP. Polystyrene was added as a low-profile additive to eliminate the polymerization shrinkage of UP during molding and tertbutyl perbenzoate (TBPB) was added as initiators. The glass fibers used were 25 mm length. The producing process of the NMP was shown in Fig. 10. Mixture of the NMFs and CaCO$_3$ were premixed in a double Z-kneader. A solution composed of UP, polystyrene, TBPB, zinc stearate and pigment was stirred for 10 min with a high shear

mixer. Then, the resin paste was added to the double Z-kneader. After 15 min of kneading, the glass fibers were added to the kneader. After the NMFs, CaCO$_3$ and glass fibers were saturated with resin, the resulting compound was called "non-metallic dough". Finally, the non-metallic dough was hot-pressed into the NMP using a self-made hot-press former shown in Fig. 11. The mold was a circle with diameter of 200 mm. The initial non-metallic dough was placed to cover 70 wt% of the mold surface to make a final plate with a thickness of 4 mm. The surface temperatures of the top and bottom molds were, respectively, $150 \pm 1\,°C$ and $145 \pm 1\,°C$. The processing time was 5 min and the hydraulic pressure was 6 MPa.

Microscopic observation revealed that NMFs with particle size from 0.3 to 0.09 mm contained predominantly sheet NMFs, with the majority of fibers being encapsulated in resin as shown in Fig. 12a and b. The NMFs from 0.09 to 0.07 mm consisted of fiber bundles and resin sheet as shown in Fig. 12c. The surfaces of fiber bundles were clean as it had been liberated from epoxy resin. The NMFs shorter than 0.07 mm consisted of single fiber resin powder as shown in Fig. 12d. A small quantity of Cu particles (1.76 vol%) existed. Lengths of short glass fiber were less than 0.2 mm. However, the differences of shapes and compositions among the NMFs with different particle sizes are determined by intrinsic structure of PCBs and the two-step crushing process. Fig. 13 shows the inner structures of the NMP with different particle sizes of NMFs. It indicates that the matrix of the NMP with short NMFs (Fig. 13b) was flatter than that with large NMFs (Fig. 13a). At the same time, the filler agglomeration was seen in Fig. 13 a, and deep void was generated near the glass fibers. During the mixing, the liquid polyester resin was able to coat the NMFs and flow into the pores between the fillers. However, the liquid resin just spread out to the surfaces of the fillers and did not fill the interstices completely when particle size of NMFs was too big. After non-metallic dough was molded, the interstices in the matrix would lead to poor performance of the NMP. Shortest NMFs (<0.07 mm) and glass fibers were homogeneously dispersed in the matrix as shown in Fig. 13b, which showed good adhesion between the fillers and resin. This may be due to short NMFs aiding the resin ingress into the voids among the fillers. After curing, the resin is locked into the NMFs, CaCO$_3$ and glass fibers, providing a good mechanical bond. Mechanical properties and morphology after flexural fracture of the NMP are shown in Figs. 14 and 15, separately. It has been found that the NMFs with particle size from 0.3 to 0.15 mm are in the form of fiber bundles, with the majority of fibers being encapsulated in resin. NMFs shorter than 0.07 mm consist of single glass fiber and resin powder. When NMFs content was 20 wt%, the NMP with particle size of NMFs less than 0.07 mm, has excellent mechanical properties, which results
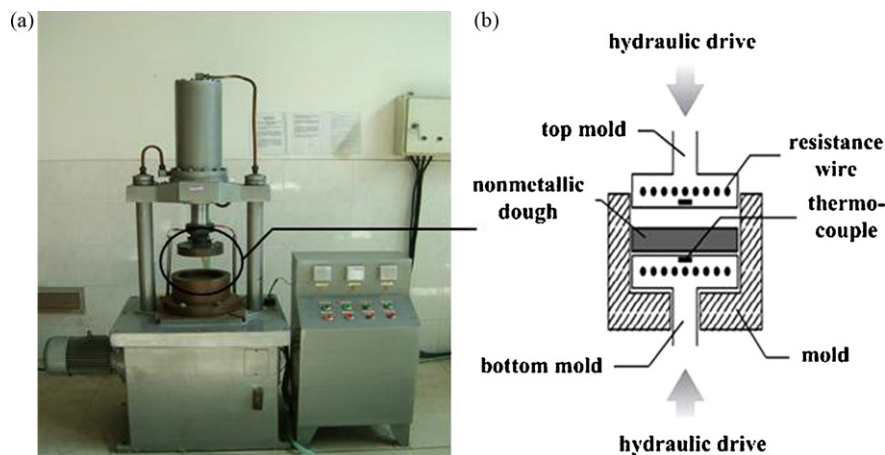

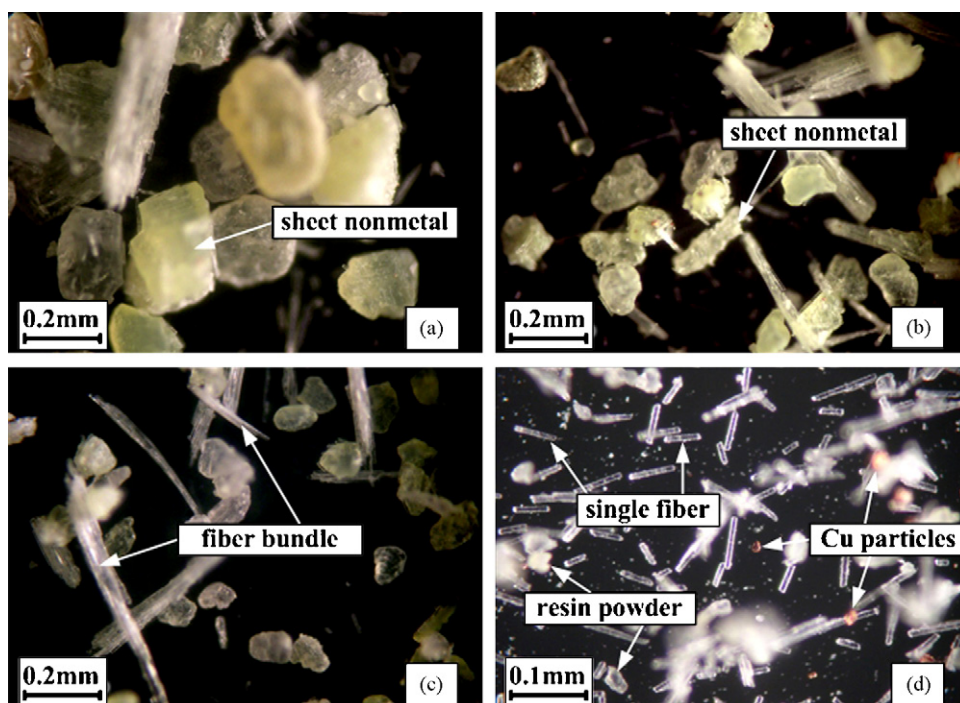**Fig. 11.** (a) Hot-press former and (b) the principle of the mold [37].

Fig. 12. Micrographs of the NMFs with different particle sizes: (a) 0.3–0.15 mm; (b) 0.15–0.09 mm; (c) 0.09–0.7 mm; (d)<0.07 mm [37].
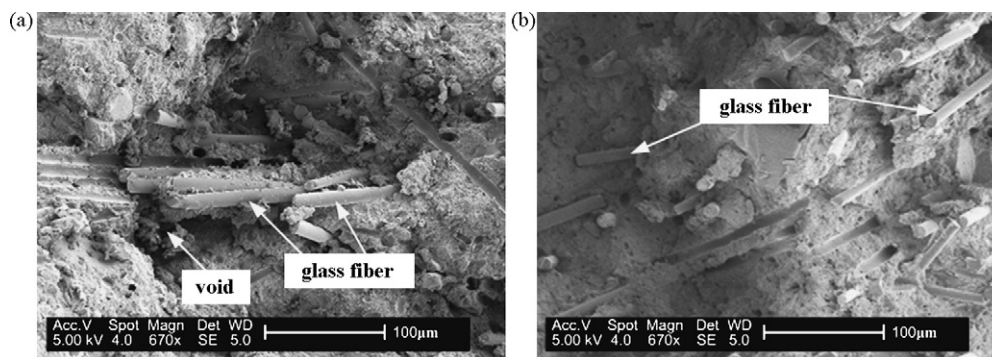

Fig. 13. The inner structure between filler and matrix in the NMP with different NMFs: (a) 40 wt%, 0.3–0.15 mm; (b) 40 wt%, <0.07 mm [37].

in a flexural strength of 68.8 MPa and a has Charpy impact strength of 6.4 kJ/m^2. This novel technique offers a possibility for recycling of non-metallic materials of PCBs and resolving the environmental pollutions during recycling of PCBs. The specimens of the NMP are shown in Fig. 16. The NMP can be used to produce different types of value-added products such as sewer grate (Fig. 17), park benches, fences and trays (seen in Fig. 18). The NMP can also be in place of wooden products since it has better mechanical performance and chemical resistance. So there is no doubt that the technique has a potential prospect in the industry of recycling non-metallic materials of PCBs.

Epoxy resins (ERs) are widely used nowadays in many applications that range from common adhesives and sealants to the matrix in high-performance composite materials. The use of epoxy resin as the matrix for fiber-reinforced composites in structural applications has been increased significantly [44–47]. Yokoyama and Iji investigated the use of the NMFs as filler for resin-type construction materials consisting of bisphenol A-type epoxy resin and an amine-type curing agent, and compared the mechanical properties of these materials with those of reference materials with silica powder [48]. The influence of the surface treatment on the NMFs was also examined. An epoxy or amino silane-coupling agent was

added to the NMFs at 1 wt%, and the mixed sample was heated at 100 °C for 1 h. As shown in Table 8, the strength properties of the mold sample of the compound with the NMFs were sufficient for use as a construction material, but a little inferior to those of the reference materials with the silica powder. The strength properties were improved by the surface treatment with the silane-coupling agents. The viscosity for the compound comprising the NMFs and the epoxy resin increased considerably more than that of the reference compounds comprising the silica powder and the epoxy resin.

Table 8
Use of the NMFs as a filler for epoxy resin [48].

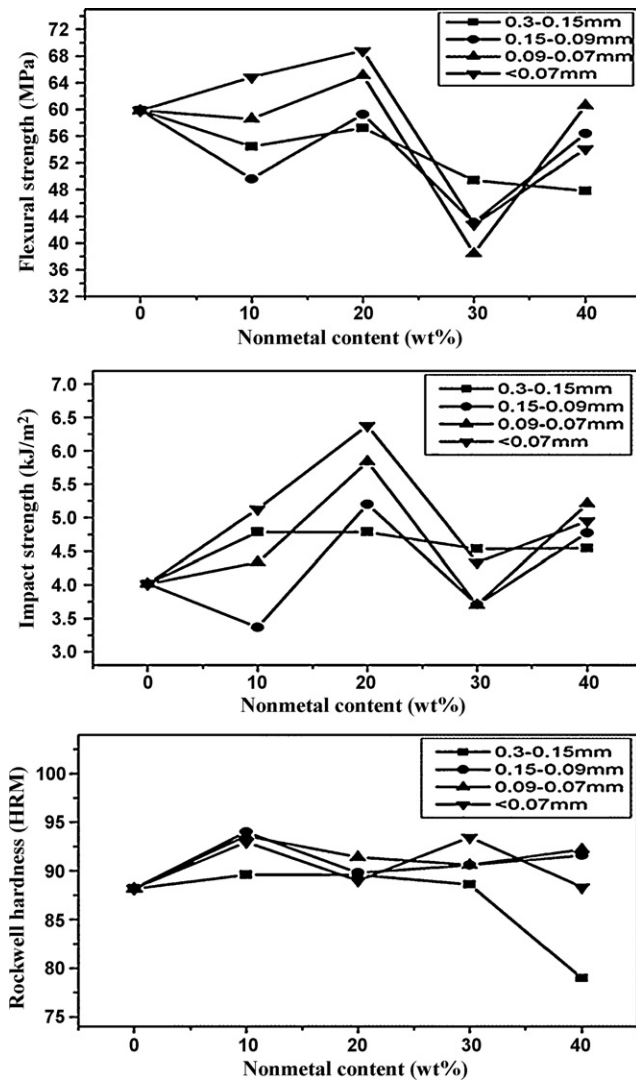| Filler	Flexural strength (kgf/cm^2)	Charpy impact strength (kgf cm/cm^2)	Viscosity (Poise)
Silica 30 wt%	1040	1.4	96
50 wt%	1070	1.5	240
NMFs 30 wt%	860	1.2	116
40 wt%	780	1.1	294
50 wt%	890	1.2	1380
Epoxy silane treatment	1020	1.2	1600
Luiiino silane treatment	970	1.1	1420

Fig. 14. Variation in mechanical properties of different particle size NMFs with varying content [37].

This viscosity increase was probably due to the difference in the specific gravity between the molding resin (1.8) and the silica powder (2.2).

Mou and his colleagues used the NMFs to produce composite boards with ERs as an adhesive [49]. In fact, this is also an application of the NMFs to be used as filler for ERs. The main components in composite boards are shown in Table 9. The products are shown in Fig. 19. Composite boards are used extensively in many fields including automobiles, furniture, amusement equipment, and decorative materials. The most attractive aspect of making composite boards from NMFs is the potential economic benefit. In general, products made from composite boards are high-value products with large profit margins. A wide variety of products can be made from composite boards for various applications.

Table 9
Main components in composite boards [49].

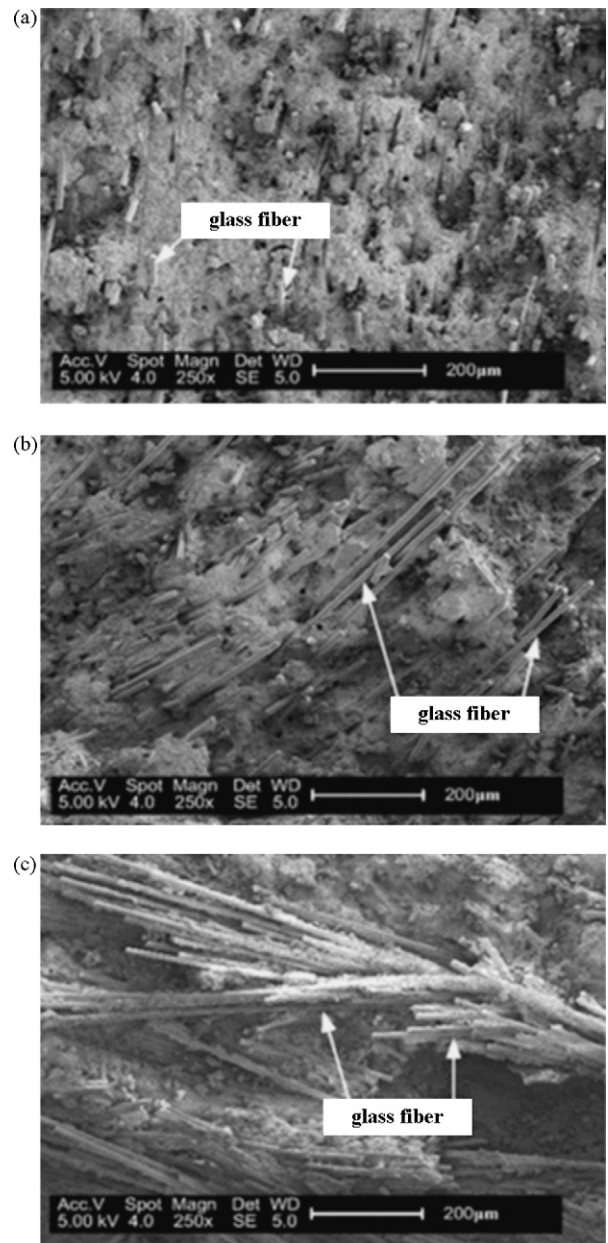| Ingredients	Ratio (wt%)
Glass fiber cloth	30–45
Epoxy resin	35–40
Fillers	5
NMFs	15–30

Fig. 15. SEM photographs of the specimens filled with the NMFs after flexural fracture: (a) without the NMFs; (b) 20 wt%, <0.07 mm; (c) 40 wt%, 0.3–0.15 mm [37].

3.2. Recycling the NMFs from waste PCBs as a reinforcing filler for thermoplastic resin matrix composites

Composite materials based on thermoplastic matrices are of key interest in many fields of engineering application. Major advantages are their technological and ecological properties and potentials. The physical profile of properties can be attained both by the choice of components and by a variation of the materials morphology [50]. Polypropylene (PP) as one of the most important commodity polymers is widely used in technical applications. Because of its good processability, great recyclability and low cost, PP has been found in a wide range of applications in the packaging, textile, automobile industries and furniture industries [51–53]. However, owing to its low strength, low modulus and high notch sensitivity, the usefulness of PP as an engineering thermoplastic is still limited. To expand the range of applications, the challenge of increasing the strength and modulus of PP has aroused considerable interest. Filling PP with

Fig. 16. The specimens of the NMP [37].

rigid inorganic particles is an effective, economical, and convenient way to enhance the strength and rigidity [54–56]. The feasibility of using the NMFs as reinforcing fillers in PP composites is studied by using mechanical and vicat softening temperature (VST) tests by Zheng et al. [38]. In their study, the waste PCBs are from a personal computer PCBs factory (without electronic elements) and consist of a woven glass fiber mat impregnated with thermoset resins (epoxy resin or phenolic resin, etc.). The process technology for mechanical recycling PCBs contains two-step crushing and air separation. The PCBs are firstly pulverized in a process consisting of a coarse-crushing step and a fine-pulverizing step. Then, air classifier is used to separate the MFs from the NMFs. After being separated, the NMFs are screened by a series of sieves with holes of 25, 80 and 150 meshes. To ensure the surface smoothness, the NMFs with particle sizes of 25–80 (coarse), 80–150 (medium) and less than 150

Fig. 17. Sewer grate made of the NMP.

Fig. 18. Trays made of the NMP.

meshes (fine) are selected and compounded in the PP composites. The NMFs particles, which are 25–80, 80–150 and less than 150 meshes, are selected for making composites. To improve the dispersion of NMFs particles in PP matrix and the compatibility between the NMFs and matrix, all the NMFs are modified with 1.0 wt% content of silane-coupling agent KH-550. PP powder S1003 is used as the matrix polymer. The PP powders and the modified NMFs particles are dried at 80 °C for 2 h. Then, the dried NMFs particles and PP powers are stirred and mixed by using high-speed mixer. The NMFs/PP blends are extruded into thread with a screw extruder. The extrudate is pelletized, dried for 2 h at 90 °C, and injected into standard samples. Fig. 20 shows the whole fabrication procedure of the NMFs/PP composites. Mechanical properties and the characteristics of VST of the NMFs/PP composites are shown in Figs. 21–23, respectively.

The mechanical test shows that both tensile and flexural properties of the NMFs/PP composites can be significantly improved by adding the NMFs into PP. The maximum increment of tensile strength, tensile modulus, flexural strength and flexural modulus of the PP composites is 28.4%, 62.9%, 87.8% and 133.0%, respectively. As much as 30 wt% NMFs recycled from waste PCBs can be added in the PP composites without violating the environmental regulation. The VST test shows that the presence of NMFs can improve the heat resistance of the non-metals/PP composites for their potential applications. The optimum particle is the fine or medium NMFs
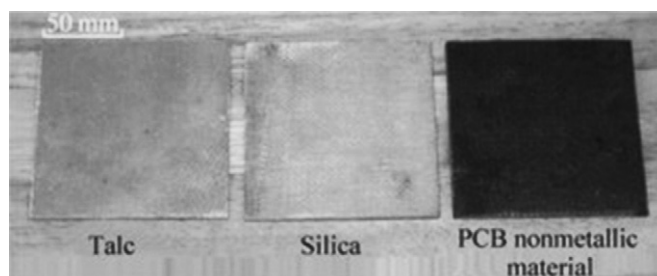

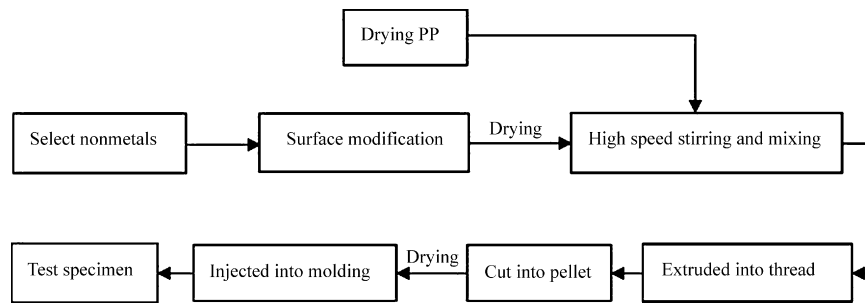**Fig. 19.** Composite boards made from talc, silica, and the NMFs [49].

Fig. 20. The process of the preparation for the NMFs /PP composites [38].
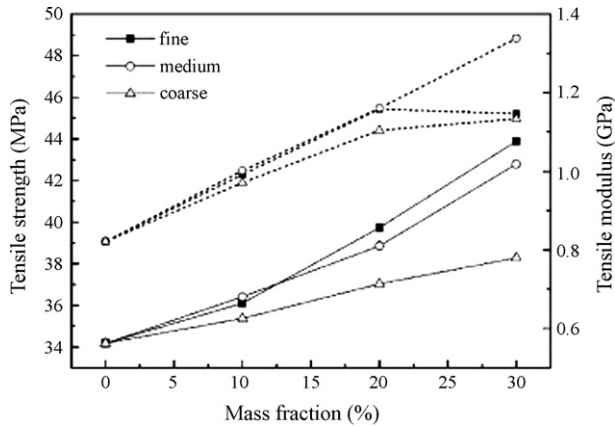

Fig. 21. (—) Tensile strength and (- - -) tensile modulus of the NMFs/PP composites [38].

recycled from waste PCBs, and the optimum content of the non-metals is 30 wt% basing on the comprehensive consideration.

3.3. Recycling the NMFs from waste PCBs as a raw material for concrete

Siddique et al. reviewed the use of recycled plastic in concrete [57]. They have summarized and concluded various aspects on plastics and its usage in concrete. As one of the plastic wastes to a certain extent, the NMFs can also be used with some effectiveness as a partial replacement of inorganic aggregates in concrete applications to decrease the dead weight of structures and increase properties of concrete such as compressive strength, splitting tensile strength, modulus of elasticity, impact resistance, permeability, and abrasion
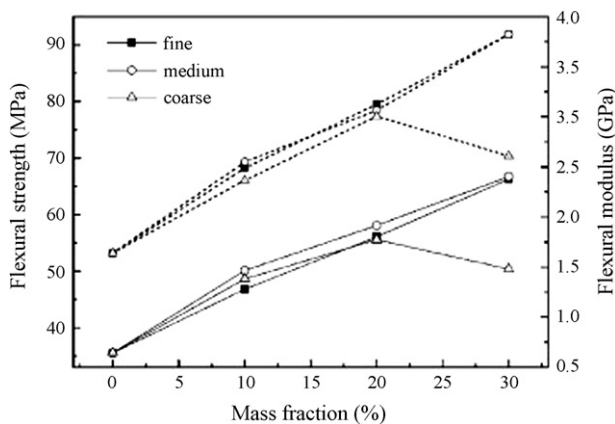
resistance. Niu and Li used cement solidification to recycle waste PCBs [58], which actually is a method to use the waste PCBs as a raw material for concrete. In their study, the materials in the specimens included cement, sand, shredded PCBs, and water. The shredded PCBs played a role as the coarse aggregate in concrete. To achieve the maximum inclusion of PCBs and minimum use of cement, the ratios among these materials were optimized by trial and error. The final ratios (weight basis) used were water/cement 1.0, sand/cement 2.5, and PCBs/cement 1.5. The procedure for making the specimens was in compliance with the ASTM C-192 standard practice for making concrete test specimens except that the shredded PCBs were used in the place of the coarse aggregate. The cement and sand were first mixed thoroughly by hand in a stainless steel bowl. Then the shredded PCBs was added and mixed. The water was added at the last and was mixed until the mortar was homogeneous in appearance and ready for molding. The molds were made of high-density polyethylene (HDPE) with an inner diameter of 76.2 mm and a height of 152 mm. The mortar was placed in the mold using a scoop in layers of 50 mm and each layer was compacted by hand for a minimum of 25 strokes. After the molds were filled, they were capped by a plastic cover that could maintain water-tightness of the mold for setting. The setting period was 24 ± 8 h for the Portland cement specimen and 72 ± 8 h for the slag cement specimens because the setting for the latter was much slower. After the setting periods, the molds were removed and the cylindrical specimens were continually cured at the room temperature ($22 \pm 2\,^{\circ}$C) in closed plastic bags where the relative humidity was maintained at above 95%. The curing time was 7 days for the specimens to be used for dynamic leaching test and 28 days for those to be used for compressive strength test. For comparison purpose, blank specimens were made. There were no PCBs in the blanks and gravel was used as the coarse aggregate. The water/cement and sand/cement ratios in the blanks
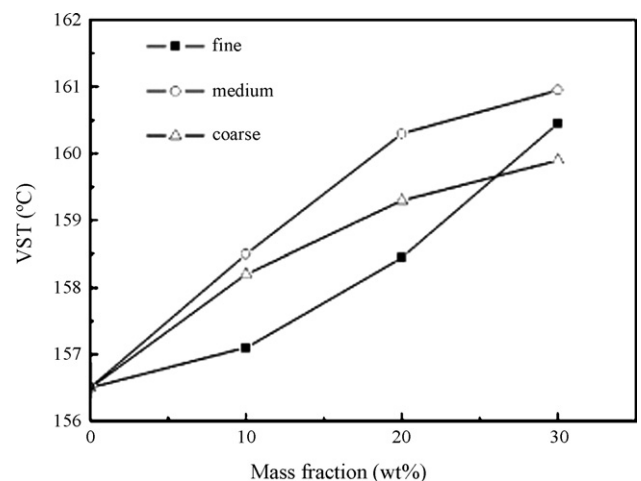

Fig. 22. (—) Flexural strength and (- - -) flexural modulus of the NMFs/PP composites [38].

Fig. 23. Vicat softening temperature (VST) of the NMFs/PP composites [38].

were the same as in the PCB-containing specimens, but a higher gravel/cement ratio of 1.7 was used for the blanks in order to achieve the same volume fraction as PCBs in the specimens. The procedure for producing the blanks was the same as for the PCB-containing specimens. The cement solidification was found to be an effective way to turn the PCBs into strong monoliths with high compressive strengths and impact resistance. Both Portland cement and slag cement showed high effectiveness in this treatment. Since the NMFs is part of the waste PCBs, their study in fact gives a referable method to recycle the NMFs as a raw material for concrete, which we believe is a more practical solution to the treatment of the waste PCBs than to use the whole waste PCBs without separation process to produce concrete.

Lightweight concrete is extensively used for the construction of interior and exterior walls of buildings for the case where the walls are not designed for lateral loads [59]. This is due to the special characteristics of lightweight concrete. At present, non-structural lightweight concrete block can be produced commercially up to a density of $600 \, kg/m^3$ which is only 1/4 of normal weight concrete and only 1/3 the normal weight of ordinary brick. Second, its thermal conductivity is about 0.089–0.150 W/m K, which is only 1/10 of the brick wall. Its compressive strength is in the range of 2.5–10.0 N/mm². Bricks are typically used for non-load-bearing walls, and their compressive strength is not greater than 3.0 N/mm². Therefore, the utilization of lightweight concrete for wall is superior to bricks. Panyakapo and Panyakapo have reused thermosetting plastic waste for lightweight concrete [59]. In their study, the melamine waste, which is also is a kind of thermosets used in PCBs, was selected for application in the mixed design of concrete. It was found that the ratio of cement, sand, fly ash, and melamine waste equal to 1.0:0.8:0.3:0.9 is an appropriate mix proportion. The results of compressive strength and dry density are 4.14 N/mm² and 1395 kg/m³, respectively. This type of concrete meets most of the requirements for non-load-bearing lightweight concrete according to ASTM C129 Type II standard. Their study indicated that use waste thermosets to produce lightweight concrete is promising method. The NMFs is a mixture of waste thermosets, glass fibers and other components, therefore, it can replace the melamine waste to produce lightweight concrete.

Mou et al. adopted this reusing conception for recycling the NMFs as a raw material for concrete and put this application forward with detailed flexural and compressive strength testing [60]. Their testing results are shown in Figs. 24 and 25. The results show that NMFs improved compressive and flexural strength of the concrete if they are properly mixed. The key factor is to find an optimal mixing ratio of resin.

3.4. Recycling the NMFs from waste PCBs as a modifier for viscoelastic materials

Yokoyama and Iji have investigated using the recovered NMFs as a filler for viscoelastic materials made of epoxy resin compound by comparing the powder with ordinary fillers, such as talc, calcium carbonate and silica [48]. The epoxy resin compound comprised an epoxy resin matrix (48 wt%), a hardener (20 wt%) and a filler (32 wt%). The resin matrix comprised a bisphenol A type epoxy resin (82 wt%), a diluent (16.5 wt%), an epoxy silane-coupling agent (0.5 wt%), a leveling agent (0.5 wt%) and a fine silica powder (0.5 wt%), and the hardener was an aliphatic polyamine type. Mechanical strength and thermal expansion properties were determined for a mold sample of the compound which was cured at 23 °C for 7 days. Viscosity was measured for the epoxy resin compound without the hardener. Adhesive strength was determined for a sample comprising two ferric boards bonded with an epoxy resin compound. This resin compound comprised the epoxy resin matrix (48 wt%), a filler (30 wt%), and a polyaminoainide-type hard-
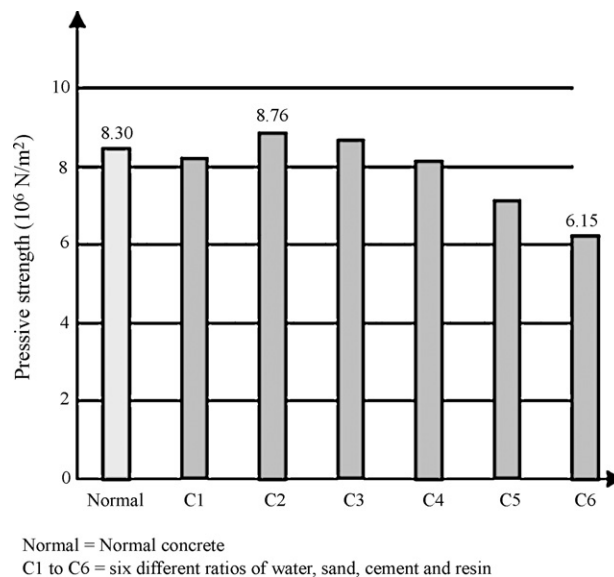
Fig. 24. Compressive strength comparison between normal concrete and concrete produced with the NMFs [60].

ener (22 wt%); and was cured at 23 °C for 7 days. As shown in Table 10, the NMFs was found to improve the mechanical strength and thermal expansion properties of the epoxy resin mold with the NMFs more effectively than talc, calcium carbonate and silica. This improvement in the properties was probably due to the compatibility between the NMFs and the epoxy resin matrix, and also because of the inclusion of glass fiber. The viscosity of the compound with the NMFs was comparable to that of the compound with talc, and was found to be greater than that of the compound with either calcium carbonate or silica. This viscosity property of the NMFs is useful in preventing the compound from dripping. The adhesive strength of the epoxy resin mold with the NMFs was sufficient, i.e., it was almost equal to that of the mold with either talc, calcium carbonate or silica (Table 11).

Asphalts are widely used in road paving. But unmodified asphalts are highly susceptible to changes in temperature due to their rheological properties. To accommodate ever-increasing traf-
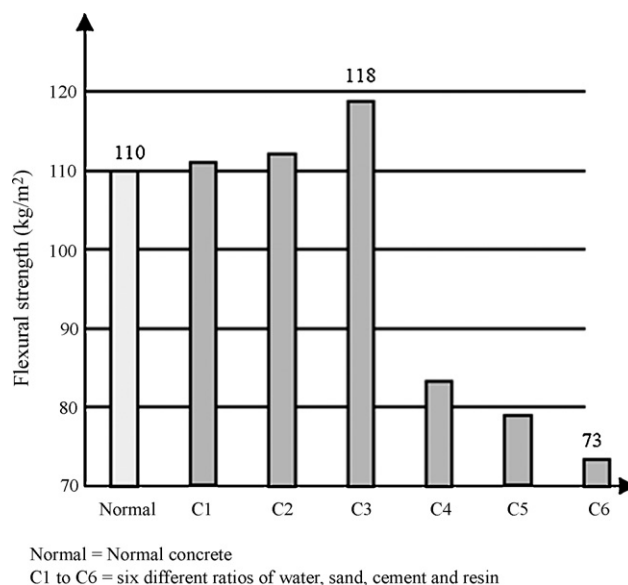

Fig. 25. Flexural strength comparison between normal concrete and concrete produced with the NMFs [60].

Table 10
Properties of the epoxy resin products (paints) [48].

Filler	Average particle size (μm)	Viscosity (Pa s)	Tensile strength (kgf/cm^2)	Charpy impact strength (kgf cm/cm^2	Coefficient of linear thermal expansion ($\times 10^{-5}$)
Calcium	9.2	7.2	336	2.37	–
Carbonate	2.6	25.8	477	2.45	14
Talc	11	69.2	280	2.50	9.5
Silica	10	7.2	428	1.64	11
NMFs	44	75.2	662	3.04	–
	20	66.2	628	3.15	–
	13	63.2	589	3.60	5.0

fic loadings in different climatic environments and to resist failures such as permanent deformation, cracking and water damage, major emphasis has been placed on improving the performance of asphalt [61]. Polymeric fibers are suitable for asphalt modification and are also used at low volume fractions. Mineral fillers are used in spherical form, and depending on applications can be as high as 25–30%. Each of them also cannot improve all aspects of asphalt performance at the same time, and much more research is required to accommodate ever-increasing traffic loadings in different climatic environments and to resist failures. The use of waste polymers as asphalt modifiers is considered a rather new and interesting way of modification because it involves two important aspects which are waste material utilization and asphalt property enhancement. The glass fibers and resins powder contained in the NMFs can be used to strengthen the asphalt. The advantage, compared to polymeric fibers particulate inorganic fillers, is that the cost of the NMFs can be considered as zero (maybe) because they are unwanted waste from PCBs recycling plants otherwise they are expensive for the treatment in land filling. On one hand, the glass fibers and resins powder contained in the NMFs strengthen the asphalt by composition effect; on the other hand, adding of the NMFs to asphalt reduce the cost of asphalt whose usage amount is very large. Therefore, asphalt modification with the NMFs maybe a promising choice and is a win–win gain from the environmental and economical viewpoints. Viscosity, penetration, ductility and softening point are the classical measurements for asphalt and these can evaluate the permanent deformation, cracking and other damages to asphalt. Rheology is the study of deformation and flow of matter. Complex modulus, phase angle, stiffness ($S(t)$) and the rate of change of that stiffness (m-value) are measured in Superpave. The effect of shape, size distribution and volume fraction of the NMFs on rheology of asphalt (viscoelastic matrix) is very important.

Since NMF is a waste that needs treatment, maybe the modification effect of asphalt with the NMFs will not be as comprehensive as that with other high-performance polymers. We consider the high-temperature performance enhancement of asphalt by the NMFs modification is more practical. If necessary, other modifiers can also be added to the NMFs modified asphalt to obtain an overall improvement in performance of asphalt. From the environmental protection and resource-saving viewpoints, the asphalt modification with the NMFs is reasonable and significant.

Table 11
Properties of the epoxy resin products (adhesives) [48].

Filler	Average particle size (μm)	Adhesive strength (tensile shear strength) (kgf/cm^2)
Calcium carbonate	2.6	157
Talc	11	138
Silica	10	151
NMFs	44	158
	20	160
	13	152

3.5. Perspectives on physical recycling of the NMFs from waste PCBs

Physical recycling of the NMFs is adopted in mechanical recycling of waste PCBs. Mechanical processing, based on the characterization of WEEE, provides an alternative means of recovering valuable materials. Mechanical processes, such as screening, shape separation, magnetic separation, Eddy current separation, electrostatic separation, and jigging have been widely utilized in recycling industry. However, recycling of WEEE is only the beginning [11]. The basic topic in physical recycling of the NMFs is how to use the NMFs as effective, cheap and safe filler for different materials. Recycling the NMFs is much more difficult than recycling routine wastes because the compositions of the NMFs are diverse and complex and even toxic, which has been presented in the analysis of compositions of the waste PCBs and the NMFs. Therefore, the conventional methods of recycling of routine wastes are not sufficient for the recycling of the NMFs which should be regarded as hazardous materials. All the physical recycling methods reviewed in this paper are believed to be effective to recycle the NMFs.

The advantages of physical recycling methods are that the processing is relatively simple, convenient, and environmentally sound, the equipment invests and energy cost are low and the potential application of products made from the recycled NMFs is diversified. There are still some challenges in physical recycling methods of the NMFs, which are how to get a clean separation between the MFs and NMFs from waste PCBs, how to enhance the compatibility between the NMFs and the matrix materials, how to prevent the hazardous substances from leaching out of the products to the least extent, how to persuade the public to use the products made from recycled materials that have passed the relevant environment safety tests, etc. More work should be done to develop comprehensive and industrialized usage of the NMFs recycled by physical methods. In sum, physical recycling of the NMFs is a promising recycling method without environmental pollution and with reasonable equipment invests and low energy cost.

4. Chemical recycling of non-metallic fractions from waste PCBs

Chemical recycling is to decompose the waste polymers into their monomers or some useful chemicals by means of chemical reactions. In this review, chemical recycling consist of pyrolysis process, gasification process, depolymerization process by using supercritical fluids and hydrogenolytic degradation. In fact, the chemical recycling of non-metallic fractions from waste PCBs is the process which is the separation of the NMFs and the MFs from waste PCBs and the upgrading of the products. The refining of the products (gases and oils) is included in the chemical recycling process, however, all the research at present concentrates on the separation and upgrading processes, and the refining process can be done with conventional refining methods in chemical plants.
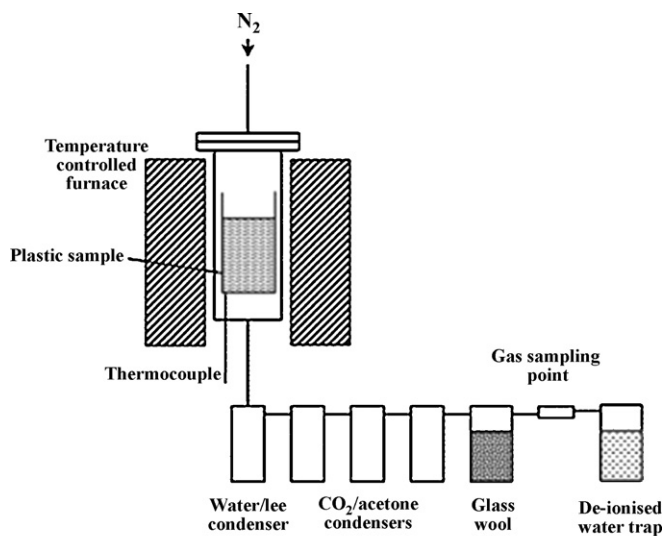
Fig. 26. Schematic diagram of the fixed bed reactor [62].

4.1. Recycling the NMFs from waste PCBs by pyrolysis processing

Pyrolysis is a chemical recycling technique that has been widely researched as a method of recycling synthetic polymers including polymers that are mixed with glass fibers. Pyrolysis of polymers leads to the formation of gases, oils, and chars which can be used as chemical feedstocks or fuels. Additionally, the pyrolysis process, if the temperature is high enough, will melt the solder used to attach the electrical components to the printed circuit boards. The combination of the removal and recovery of the organic fraction of printed circuit boards and the removal of the solder should aid the separation of the metal components from the organic material. Hall and Williams investigated the pyrolysis of waste PCBs from waste computers, televisions, and mobile phones in a fixed bed reactor with the aim of separating and recovering the organic and metallic materials [62]. In their study, a selection of printed circuit boards from each of the three waste classes was pyrolysed at 800 °C and the pyrolysis products were analysed using GC–FID, GC–TCD, GC–MS, GCECD, ICP–MS, and SEM–EDX. The fixed bed reactor is shown in Fig. 26, which measured 260 mm in length by an internal diameter of 44.5 mm and was externally heated by a 1.5 kW tube furnace. The computer printed circuit boards pyrolysed to form an average of 68.9 wt% residue, 22.7 wt% oil, and 4.7 wt% gas. Pyrolysis of the television circuit boards led to an average mass balance of 60.0% residue, 28.5% oil and 6.5% gas and pyrolysis of the mobile phone circuit boards led to an average mass balance of 82.2 wt% residue, 15.2 wt% oil and 2.3 wt% gas. The composition of the pyrolysis gases, an analysis of the metals present in the char, quantification of the major products in the oil produced by the pyrolysis of printed circuit boards at 800 °C in a fixed bed reactor are shown in Tables 12–14, respectively. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethyl) phenol, and p-hydroxyphenol, as well as bisphenol A, tetrabromobisphenol A, methyl phenols, and bromophenols. The pyrolysis oils also contained significant concentrations of organo-phosphate compounds and a number of tetrabromobisphenol A pyrolysis products were also identified. The pyrolysis residues were very friable and the organic, glass fiber, and metallic fractions could easily be separated and the electrical components could easily be removed from the remains of the printed circuit boards. The ash in the residue mainly consisted of copper, calcium, iron, nickel, zinc, and aluminium, as well as lower concentrations of valuable metals such as gallium, bismuth, silver, and gold, silver was present in particularly high

Table 12
Mass composition of the pyrolysis gases produced by each printed circuit board type on a nitrogen free basis (wt%) [62].

Component	Computers	Televisions	Mobile
H2	4.6	3.2	5.7
CO	27	21.8	36.1
CO2	51	51.5	45.8
Methane	10.3	14	6.4
Ethene	0.6	1.1	0.5
Ethane	1.9	2.7	0.6
Propene	2	1.1	2.7
Propane	1	1.6	0.4
Butene	0.8	1.8	1
Butane	0.5	1.2	0.2
Cl	0	0	0.1
Br	0.3	0.1	0.5

Table 13
An analysis of the metals present in the char produced by the pyrolysis of PCBs at 800 °C in a fixed bed reactor (mg/kg) [62].

	Computers		Television		Mobile phone	
	>600 μm	<600 μm	>600 μm	<600 μm	>600 μm	<600 μm
Li	6	13	<5.6	<5.6	13	15
Na	474	1,206	140	554	897	1,197
K	151	519	1332	697	236	347
Mg	448	1,317	414	4,315	635	947
Ca	25,167	50,647	2578	24,905	33,901	40,984
Sr	185	658	<5.6	20	334	372
Ba	618	8,050	41	285	10,739	6,786
Cr	42	268	118	787	1792	139
Mn	372	177	674	592	654	569
Fe	69,729	11,355	159,671	31,461	15,089	5366
Co	12	<5.6	93	56	64	39
Ni	10,660	1,331	24,388	1,863	13,454	6,870
Cu	242,986	167,105	260,404	185,190	333,228	323,163
Zn	13,139	700	14,695	10,149	1,011	960
Ga	45	27	94	29	210	184
Al	10,479	21,618	3215	6426	14,949	18,333
In	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6
Bi	301	77	75	68	<5.6	<5.6
Pb	128,242	21,466	76,900	91,577	1405	2495
Cd	8	<5.6	13	<5.6	<5.6	<5.6
Ag	6458	800	15,020	1164	8118	4,125
Sb	<5.6	7	<5.6	12	44	8
Au	6	211	<5.6	<5.6	18	28
Hg	7	6	6	<5.6	12	7
Pd	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6
Ti	19	70	65	90	1508	708

Table 14
Quantification of the major products in the oil resulting from the pyrolysis of PCBs at 800 °C in a fixed bed reactor (%) [62].

|	Computers	Television	Mobile
Phenol	25.23	10.06	38.49
2-Methylphenol	1.04	1.60	1.07
4-Methylphenol	1.45	2.20	0.31
2,6-Dimethylphenol	0.27	0.50	0.15
2-Ethylphenol	0.22	0.20	0.24
4-Ethylphenol	0.47	0.26	0.61
4-(1-Methylethyl)phenol	8.61	1.26	16.11
p-Hydroxydiphenyl	1.47	0.08	2.87
Bisphenol A	1.38	0.11	0.67
Triphenyl phosphate	0.92	4.25	0.09
o-Cresyl phosphate	0.55	0.00	0.00
m-Cresyl phosphate	0.10	0.00	0.00
2,4-Dibromophenol	0.03	0.35	0.01
2,6-Dibromophenol	0.34	0.56	0.10
TBBPA	0.0006	0.0013	0.000
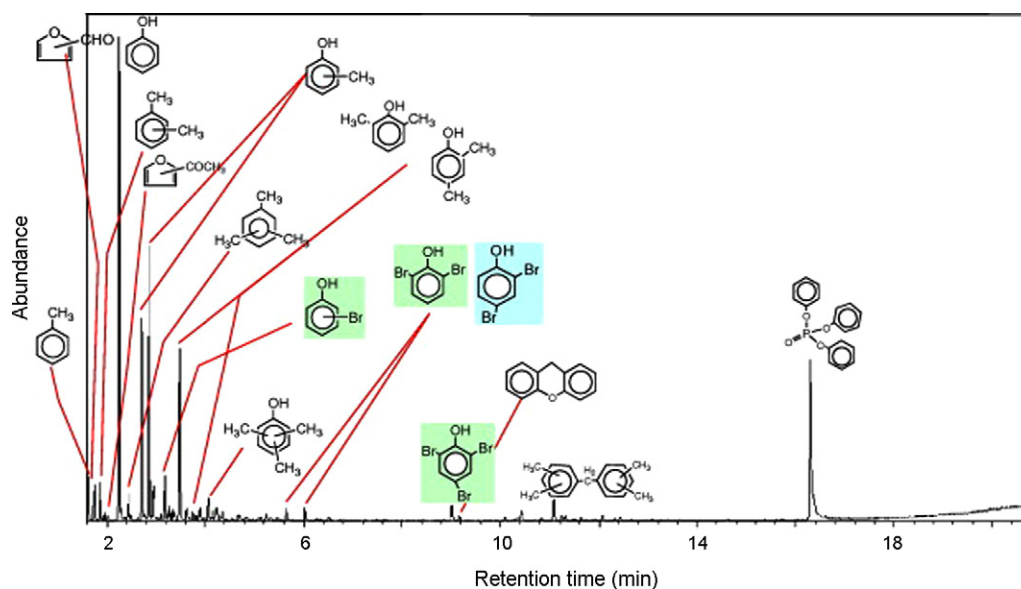
Fig. 27. GC–MS of the product oil after the degradation of TBBA containing paper laminated phenol resin [63].

concentrations. Many other metals were also identified in the ash by ICP–MS and SEM EDX. The pyrolysis gases mainly consisted of CO_2 and CO but all of the C_1–C_4 alkanes and alkenes were present, as were some inorganic halogens.

It is important to know the behavior of halogens during degradation processes. This is true not just of the combustion process, but also the pyrolysis process and the chemical recycling of fire retardant containing materials in particular.

Tetrabromobisphenol-A (TBBA) is the most common brominated fire retardant. In a study led by Yoshioka [63], a TBBA containing paper laminated printed circuit board prepared from novolac was pyrolysed by both TGA and in a quartz glass reactor between 40 °C and 1000 °C. The GC–MS analysis of the products from the degradation of the TBBA containing PCB indicated the presence of aromatic products only. Methylated phenols and methylated benzene derivatives were the most prominent degradation products after phenol (Fig. 27). Also, brominated phenols were found among the degradation products of TBBA, with the main products being 2-bromophenol, 2, 4-dibromophenol, 2, 6-dibromophenol and 2, 4, 6-tribromophenol. Triphenyl phosphate, another phosphorous-based fire retardant, was also observed. The oily residue condensed at the exit of the reactor contained additional condensed aromatics such as methyl naphthalene and methyl anthracene, which are precursors for the formation of char. The residue was charcoal-like in appearance. The C/H ratio increased from 0.74 of the original material to 3.1 for highly condensed aromatic systems lacking in hydrogen. The bromine content decreased from 3.6 to 0.19 wt%. The results of the GC–ECD determination of the brominated organic compounds and the IC-determination of HBr are given in Table 15. Most of the bromine was released in

Table 15
Bromine disposition after the PCBs degradation [63].

Brominated product	Disposition (%)
HBr (determined by IC)	87
Brominated aromatics	14
2-Bromophenol	3.2
2,4-Dibromophenol	2.7
2,6-Dibromophenol	2.8
2,4,6-Tribromophenol	5.3
Residue	1.8
Total bromine	103

the form of HBr (87%), another 14% was bound in organic compounds, and about 1.8% of the original bromine content was left in the residue. Brominated bisphenol A (BBPA) derivatives were not observed among the products. The release of the brominated aromatics was completed below 400 °C. However, only 50% of the bromine was released as HBr at this temperature. Another 37% of HBr was released from the resin between 400 and 700 °C. The results show that brominated aromatic compounds are exclusively formed between 270 and 400 °C, and that bromine is released at higher temperatures only in the form of HBr. Phenolic products with a low bromine content can be obtained at a temperature of about 450 °C by avoiding the temperature range during which brominated aromatic compounds are formed and accelerating the fixation of TBBA in the resin by the formation of char. It was found that the TBBA containing paper laminated PCB degraded in three steps. Step one (<270 °C) consisted of the evolution of water and CO_2 from the paper laminate. In the second step, between 270 °C and 370 °C, the fire retardant decomposed, releasing HBr and brominated aromatics. In the third step, at temperatures above 370 °C, the phenol resin decomposed and char was formed. Compared to pure TBBA, which mainly produces brominated phenols, the brominated products enclosed in the char released HBr during the last degradation step as well as during the second step. Most of the bromine left the resin in the form of HBr, with about 14% of the bromine being fixed in brominated aromatics and less than 2% remaining in the residue.

Brominated epoxy resins (BERs) are a kind of most common polymers contained in waste PCBs. The pyrolysis behavior of BERs is quite important for chemical recycling of the NMFs from waste PCBs. Luda et al. studied the thermal decomposition of fire retardant brominated epoxy resins cured with different nitrogen-containing hardeners [64]. The experimental evidence points to a cooperative action of bromine and nitrogen in chain scission of brominated epoxy resins. This implies that HBr evolved from diglycidyl ethers of tertabromobisphenol A (DGETBBA) units and fixed by the amine hardener helps the scission of the C–N bond in the network. Consequently differences of 30–60 °C in thermal stability of epoxy networks have been found, depending on the hardener and significantly on its ability as a base scavenger of HBr. This possibility should be taken into consideration in defining the thermal recycling conditions: even at temperature as low as 300 °C some BER are highly unstable and can form precursors of very toxic PDDB and PBDF.
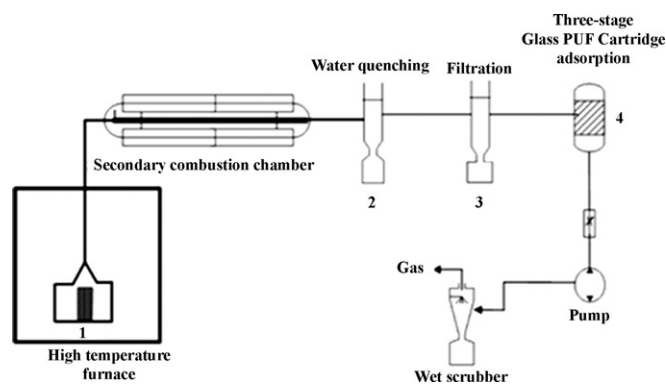
Fig. 28. High-temperature melting system: (1) bottom ash, (2) cooling unit, (3) filter, (4) glass PUF cartridge [65].

Table 16
Mean PBDD/F contents in bottom ashes ($n = 2$) [65].

Compounds	Content (ng/g)	
	P1 (850 °C)	P2 (1200 °C)
2,3,7,8-TeBDD	0.013	0.002
1,2,3,7,8-PeBDD	0.147	0.065
1,2,3,4/6,7,8-HxBDD	0.336	0.311
1,2,3,7,8,9-HxBDD	0.112	0.102
2,3,7,8-TeBDF	0.180	0.024
1,2,3,7,8-PeBDF	0.417	0.137
2,3,4,7,8-PeBDF	0.638	0.293
PBDDs	0.609	0.480
PBDFs	1.23	0.454
Total PBDD/Fs	1.84	0.935
Total I-TEQ	0.490	0.231

Due to the persistence and toxicity of PBDD/Fs, a combined controlling method to inhibit both PCDD/Fs and PBDD/Fs is of great importance for recycling the NMFs from waste PCBs by pyrolysis processing. Lai et al. studied the inhibition of PBDD/Fs formation from the pyrolysis of waste PCBs [65]. The high-temperature melting system used in their study is shown in Fig. 28. The melting system consists of a high-temperature furnace, a secondary combustion chamber, and one set of air pollution control devices (APCDs) including a cooling unit (collects the condensed water of the volatile gas), a filter (collects particles), and three-stage glass PUF cartridge adsorption (collects the gaseous phase compound). The experimental sample placed inside a graphite crucible was put in the furnace; the furnace temperature was than increased to 850 °C or 1200 °C at 6 °C min^{-1} (held for 30 min), with the secondary combustion chamber at 1200 °C. Two samples were used: (i) 30 g of flexible PCBs and (ii) 30 g of flexible PCBs and 30 g of CaO at 850 °C (denoted as P1 or A1) and 1200 °C (denoted as P2 or A2), respectively. The pump rate for withdrawing gaseous samples

Table 18
Mean PBDD/F contents in bottom ashes by adding CaO during pyrolysis ($n = 2$) [65].

Compound	Content (ng/g)	
	P1 (850 °C)	P2 (1200 °C)
2,3,7,8-TeBDD	0.001	0.001
1,2,3,7,8-PeBDD	0.001	0.001
1,2,3,4/6,7,8-HxBDD	0.075	0.005
1,2,3,7,8,9-HxBDD	0.009	0.001
2,3,7,8-TeBDF	0.003	0.004
1,2,3,7,8-PeBDF	0.023	0.003
2,3,4,7,8-PeBDF	0.060	0.016
PBDDs	0.085	0.007
PBDFs	0.086	0.022
Total PBDD/Fs	0.171	0.029
Total I-TEQ	0.040	0.010

was 10 l/min. The batch experiment was repeated twice. After the pyrolysis process, the bottom ash, fly ash, and cartridge were collected and analyzed to determine the concentrations of PBDD/Fs on the basis of the National Environment Analysis Method (NIEA M801.11B) of Taiwan, similar to USEPAB modified method 23A. The PBDD/F contents in the bottom ashes and mean emission factors (pg/g of waste) of PBDD/Fs collected by the Cooling Unit, Filter, and Glass PUF Cartridge are shown in Tables 16 and 17, respectively. Mean PBDD/F contents in bottom ashes by adding CaO during pyrolysis and mean emission factors (pg/g of waste) of PBDD/Fs collected by the Cooling Unit, Filter, and Glass PUF Cartridge by adding CaO during pyrolysis are shown in Tables 18 and 19, respectively. The results showed that the formation of PBDD/Fs during pyrolysis can be destroyed under controlled primary combustion conditions. There were two significant factors that influenced the extent of PBDD/F formation. The first factor was temperature. The results showed that, both the total PBDD/F content in the bottom ash and the total PBDD/F emission factor from the flue gas decrease by approximately 50% with an increase of the pyrolysis temperature from 850 °C to 1200 °C. The second factor was the addition of CaO. The possible mechanism involves the reaction between CaO and HBr to form the solid-phase product CaBr$_2$. Thus, the addition of CaO is effective in adsorbing HBr and results in the inhibition of PBDD/F synthesis by more than 90% and further prevents the acid gases (HCl and HBr) that corrode the equipment.

The pyrolysis efficiency can be improved and the temperature can be reduced by adding proper catalysts during pyrolysis. Hall et al. used a waste fluidized catalytic cracker (FCC) catalyst to pyrolyse WEEE plastics [66]. In their work, they have investigated using a zeolite-based waste FCC catalyst to remove toxic brominated compounds from the pyrolysis products of flame-retarded high-impact polystyrene and acrylonitrile–butadiene–styrene. The investigation was carried out using a fixed bed reactor, and the pyrolysis products were characterized using gas chromatography, Fourier-transform infrared spectroscopy, and ion chromatography.

Table 17
Mean emission factors (pg/g of waste) of PBDD/Fs collected by the cooling unit, filter, and glass PUF cartridge ($n = 2$) [65].

Compound	Cooling unit		Filter		Glass PUF cartridge	
	P1 (850 °C)	P2 (1200 °C)	P1 (850 °C)	P2 (1200 °C)	P1 (850 °C)	P2 (1200 °C)
2,3,7,8-TeBDD	15.3	3.62	BD[a]	0.056	4.03	6.89
1,2,3,7,8-PeBDD	57.6	21.3	1.73	2.06	31.1	27.3
1,2,3,4/6,7,8-HxBDD	66.2	23.3	7.32	7.10	54.1	34.9
1,2,3,7,8,9-HxBDD	26.7	7.47	2.39	2.61	20.7	11.2
2,3,7,8-TeBDF	15.1	4.39	BD	0.053	9.25	3.79
1,2,3,7,8-PeBDF	9.51	4.39	BD	0.387	7.89	4.53
2,3,4,7,8-PeBDF	23.8	8.98	0.557	1.04	16.1	10.9
PBDDs	166	55.7	11.4	11.8	110	80.3
PBDFs	48.0	17.8	0.557	1.50	33.0	19.2
Total PBDD/Fs	214	73.5	12.0	13.3	143	99.5

[a] BD: below detection limit.

Table 19
Mean emission factors (pg/g of waste) of PBDD/Fs collected by the cooling unit, filter, and glass PUF cartridge by adding CaO during pyrolysis ($n = 2$) [65].

| Compound	Cooling unit		Filter		Glass PUF cartridge	
	P1 (850 °C)	P2 (1200 °C)	P1 (850 °C)	P2 (1200 °C)	P1 (850 °C)	P2 (1200 °C)
2,3,7,8-TeBDD	0.023	0.010	BD[a]	BD	0.043	BD
1,2,3,7,8-PeBDD	0.038	0.043	BD	BD	0.146	BD
1,2,3,4/6,7,8-HxBDD	0.143	0.108	BD	BD	BD	BD
1,2,3,7,8,9-HxBDD	BD	0.041	BD	BD	BD	BD
2,3,7,8-TeBDF	0.754	0.010	0.038	0.017	0.153	0.037
1,2,3,7,8-PeBDF	BD	0.198	BD	BD	0.083	BD
2,3,4,7,8-PeBDF	BD	0.189	BD	BD	0.120	BD
PBDDs	0.204	0.203	0.038	0.000	0.189	0.000
PBDFs	0.754	0.397	0.000	0.017	0.353	0.037
Total PBDD/Fs	0.958	0.600	0.038	0.017	0.543	0.037

[a] BD: below detection limit.

The pyrolysis of each plastic was investigated at 410 °C and 520 °C in both the presence and the absence of the catalyst using a fixed bed reactor. It was found that the waste FCC catalyst was effective at reducing the bromine content of the pyrolysis oils, particularly during the pyrolysis of Br-HIPS. Unlike previous catalysts that have been used to reduce the bromine content of pyrolysis oil, the waste FCC catalyst did not greatly alter the pyrolysis products, therefore preserving the valuable single-ring aromatic compounds. However, it was unclear from this work exactly how the waste FCC catalyst reduced the bromine content of the pyrolysis oil.

4.2. Recycling the NMFs from waste PCBs by gasification processing

The main purpose of gasification processes in the processing of polymer wastes is the generation of synthesis gas (CO, H_2). Possible by-products in these processes are CO_2, H_2O, CH_4 and soot. The reaction temperatures range up to 1600 °C at a pressure of up to 150 bar. The correct choice of the gasification process itself may be decisive, too. The most valuable product is a hydrogen-rich synthesis gas with a high portion of reactive components (no inerts) and only minor impurities. This product is a valuable feedstock for the methanol synthesis. Fuel gas which can be classified by different caloric values is the product of the lowest value. It can be used for the generation of heat and electricity [67].

Yamawaki studied the gasification recycling technology of plastics WEEE containing brominated flame retardants [68], which gives a reference to the recycling the NMFs from waste PCBs by gasification processing. The experimental equipment shown in Fig. 29 was used as a model of the commercial-scale gasification process. The plastic sample enters from the upper part of the gasification furnace and is converted to the gas. The generated gas is led to the high-temperature furnace, and stays in this high-temperature furnace for about 2.5 s at a temperature of 1150 °C. PBDDs and PBDFs are expected to decompose at these high temperatures. PBDDs/PBDFs were decomposed by the high-temperature treatment (1150 °C and residence time of 2.5 s) to decomposition rate of 99.99% or more. The following three samples were tested: high-impact polystyrene resin containing PBDE (polybrominated diphenyl ethers, mainly decabromo diphenyloxide) as brominated flame retardant (sample 1); high-impact polystyrene resin containing brominated flame retardant other than PBDE (mainly decabromo diphenyloxide) (sample 2); ABS resin containing brominated flame retardant (sample 3). The detailed results were as follows. At sampling point S1, the toxicity equivalent quantity of PBDDs/PBDFs, using the TEF of chlorinated dioxins was 2300–7800 ng TEQ/Nm^3. At sampling point S2 the toxic equivalent quantity of PBDDs/PBDFs was decreased to 0.014–0.59 ng TEQ/Nm^3. Moreover PBBs (polybrominated biphenyls), PBPs (polybrominated phenols), PBDEs (polybrominated biphenyl ethers) and
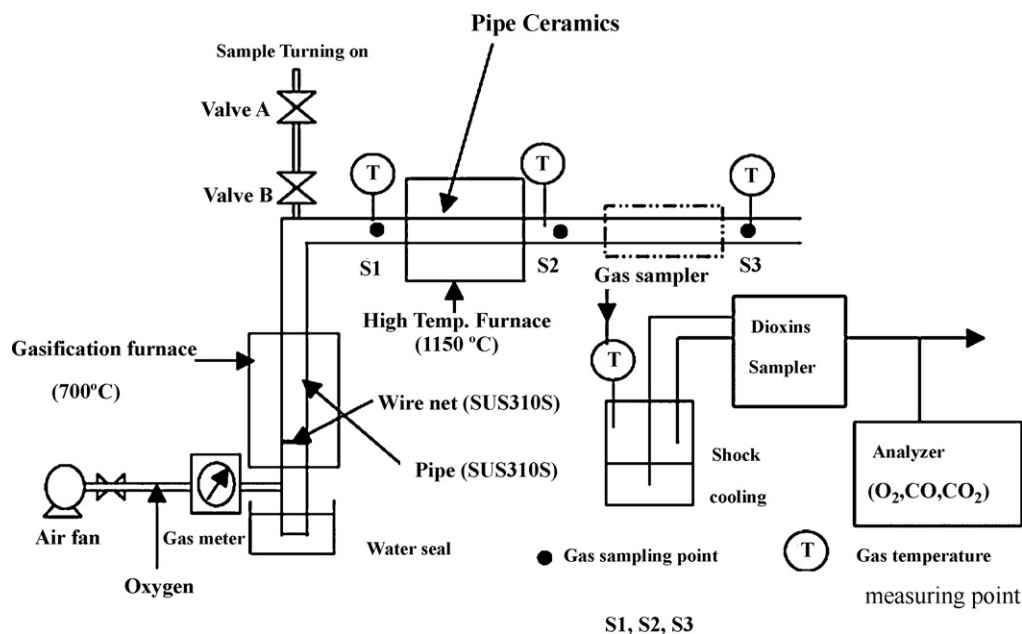
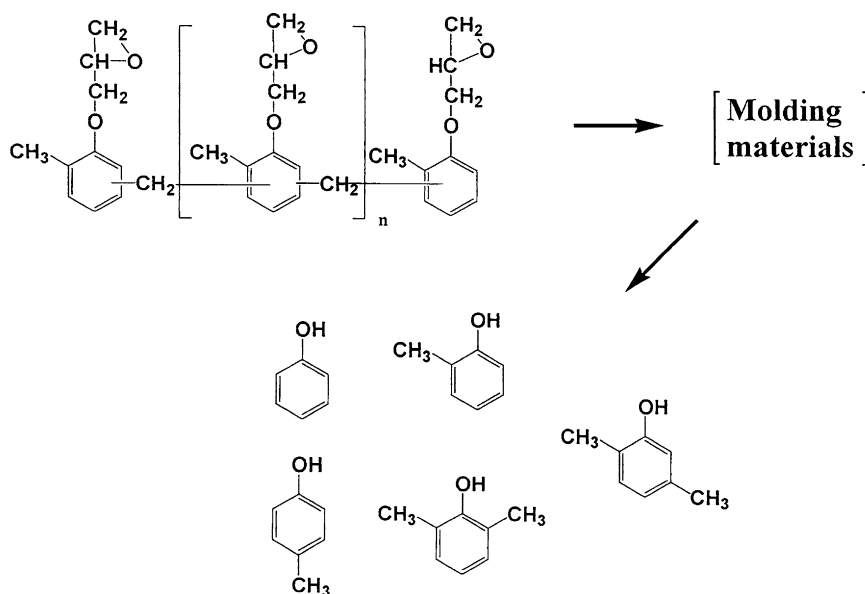**Fig. 29.** Gasification experimental equipment [68].

Fig. 30. Identified products in the decomposition reaction of molding epoxy resin at 703 K in supercritical water (SCW) [71].

TBBP-A (tetrabromo bisphenol A) which are all considered as potential precursors of PBDDs/PBDFs were decomposed by the high-temperature treatment too. After the high-temperature treatment at 1150 °C, shock cooling of gas to about 50 °C was done in this experiment. This work showed that the high-temperature treatment and shock cooling suppressed PBDDs/PBDFs emission to very low level. It is also clear from this work that at slow cooling after high-temperature treatment, PBDDs/PBDFs emission reached values 2300–4300 times higher than those reached following the fast shock cooling. This means that there was regeneration of PBDDs/PBDFs occurring during the slow cooling. During the work, almost all the bromine in the initial plastic was exhausted to the outlet of the high-temperature furnace in the gaseous state. Almost all the antimony (also contained as synergistic flame retardant) was gathered in the equipment as solid. The results show that gasification of plastic WEEE containing brominated flame retardants can be achieved to prevent the generation of brominated dioxins and to prevent the regeneration of brominated dioxins, similar to the experience with chlorinated dioxins under the proper operating conditions. Therefore, gasification of the NMFs from the waste PCBs can be considered as another chemical recycling method that can prevent of the generation of brominated dioxins. However, the relevant research at present is very few.
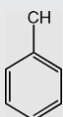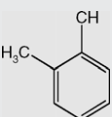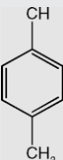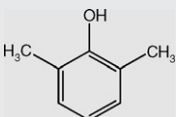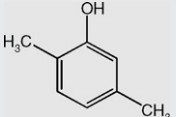
4.3. Recycling the NMFs from waste PCBs by depolymerization in supercritical fluids

A supercritical fluid is any substance at a temperature and pressure above its thermodynamic critical point. Supercritical fluids (SCFs), and especially supercritical water (SCW), are potential media for the recycling of fibres and resin since they can be inexpensive reaction media, recyclable, non-toxic and relatively easy to handle. SCW also possesses an interesting combination of properties such as low viscosity, high mass transport coefficients, high diffusivity and solvation power [69]. The critical temperature and pressure of water are 647 K and 22.1 MPa, respectively. The dielectric constant, the ion product, and viscosity of water at the critical point are 6, 10^{-12} (kW: $(mol)^2$), and 0.002, respectively. Under supercritical conditions, water, organic compounds, and gases are completely miscible. Furthermore, supercritical water is now emerging as a useful chemical medium that could provide optimum conditions for a variety of chemical reactions, including the destruction of hazardous waste.

Chien et al. used SCW to oxidize waste PCBs [70], in whose study the resins contained in the NFMs from waste were converted to CO_2, H_2O, NaBr, etc. In fact, besides being used for hydrothermal oxidation treatment of waste PCBs, SCW can be used to recycle

Table 20
Decomposition reaction of molding epoxy resin at 703 K for 1 h with 3 ml solvent in supercritical water (SCW) [71].

Solvent (additive)	Yield of identified products (wt%)					
						Total
None	1.5	2.0	0.7	0.4	0.8	5.4
1-Methylnaphthalene	1.3	2.3	0.8	0.5	1.0	5.8
Water (none)	0.7	1.5	0.3	0.4	1.0	3.9
Water (0.3 wt%NaCl)	0.8	1.5	0.4	0.3	1.0	4.1
Water (0.3 wt% Na_2CO_3)	2.6	4.5	0.7	0.5	1.4	9.6
Water (3 wt% Na_2CO_3)	2.7	4.4	0.8	0.5	1.6	9.9

the NMFs from waste PCBs by depolymerization process because it is an excellent hydrolysis reagent. Tagaya et al. have studied the decomposition reactions of epoxy resin in SCW [71]. Molding epoxy resin decomposition was carried out at 703 K for 1 h, 3 ml of 1-methylnaphthalene and 3 ml of water. The identified products in the decomposition reaction of molding epoxy resin at 703 K are shown in Fig. 30. The addition of Na_2CO_3 was shown to have a significant effect and yields increased to nearly 10% (wt%) as shown in Table 20. The addition of basic compounds such as Na_2CO_3 was effective in promoting the decomposition reaction of the resins. In the reaction of epoxy resin, the yield of identified products reached 10% for the reaction at 703 K over 1 h. The results suggest that water played an important role not only as a physically stable medium at high temperature, but also as a chemical reagent.

Possible merits of utilizing supercritical methanol over supercritical water are found in the following respects [72]. First, the operation condition will be milder because the critical temperature and pressure of methanol (T_c = 240 °C, P_c = 8.09 MPa) are lower than those of water. This would widen the selection of materials for the reactors. Second, the separation of products from the solvent is much easier than the case using supercritical water, because the boiling point of methanol is lower than that of water. Additionally, alteration or modification of the product distribution would also be expected by changing the solvent. Ozaki et al. investigated recycling of phenol resin by supercritical methanol [72]. A total of 200 mg of used phenol resin fiber (KR-0204) with a diameter of 10 μm was charged in a stainless steel autoclave (reactor volume: 200 ml) with 70 ml of methanol. Air in the inner space of the autoclave was purged by nitrogen gas at 10 MPa. After returning the pressure to ambient pressure, the reaction was started by heating of the vessel in an electric furnace. The pressure inside the vessel was monitored by a pressure gauge attached to one of the ports of the autoclave. Because of the large heat capacity of the vessel, it normally took about 260 min to attain 400 °C and 300 min to attain 420 °C. The reaction temperature was controlled by a PID controller to maintain the temperature at the preset temperature (300, 350, 400, and 420). During the reaction, the contents in the vessel were not agitated. The time period of the preset reaction temperature was varied from 30 to 150 min by fixing the reaction temperature at 400 °C. Hereafter, this time is referred to as the nominal reaction time, because the time required for heating was long. It was found that supercritical methanol could liquefy phenol resin, and the reaction was obvious above 400 °C to give a conversion higher than 80%. Both reaction conditions of a longer time at a temperature and a higher reaction temperature for a shorter time resulted in increasing the conversion. However, the former condition turned out to be favorable for obtaining a higher yield of liquid products. The liquid product was found to include phenols. The analysis of the solid products revealed a concentration of carbon atoms during the reactions.

Other supercritical fluids such as ammonia may also be suitable to convert the polymers contained in the NMFs from waste PCBs into monomers. The transformation efficiency depends on the reactions between the supercritical fluid and the function groups in the crosslinked thermosets. The critical temperature and pressure of fluids is significant when they are chosen as depolymerization reagents for recycling the NMFs from waste PCBs. The lower critical temperature and pressure of fluids means lower energy cost and equipment requirement. In water pollution controlling area, oxidation in supercritical water with air is regarded as an advanced oxidation technology. But there are no air engaged in the depolymerization of polymers process in supercritical fluids, otherwise the polymers will be oxidized to CO_2 and H_2O which have no value for the recycling purpose. Therefore, there are several challenges, such as choosing of proper supercritical fluids and additives, cost of energy and equipment investment controlling, operation parame-

ters optimization, etc., faced by using supercritical fluids to recycle the NMFs from waste PCBs.

4.4. Recycling the NMFs from waste PCBs by hydrogenolytic degradation

Hydrogenolytic degradation is an innovative recycling technique for feedstock recycling of thermosetting resins, although there is little reported study on recycling the NMFs from waste PCBs by hydrogenolytic degradation in available documents. The investigation carried out by Braun et al. has given a good reference to recycle thermosets by hydrogenolytic degradation [73].

In their investigation it was shown that many crosslinked polymers, especially epoxy resins, can be liquefied by transfer hydrogenation with various hydrogen donors. The epoxy resin crosslinked with phthalic anhydride, the phenolic resin and the melamine resin were used as materials in their study. One gram of the ground resin was put into an autoclave together with 5 g tetraline and heated for 5 h. The degradation temperature was varied between 320 °C and 410 °C. After the reactor was cooled down, the insoluble residue was weighed. The yield of the liquefied resin against the reaction temperature is shown in Fig. 31. The most important products identified were bisphenol A and its fragments phenol and *p*-isopropylphenol as well as phthalic anhydride and its fragments benzoic acid and benzene. The yield of bisphenol A reached its maximum of 11.3 wt% at 370 °C. At higher temperatures the hydrogenolysis of bisphenol A gains importance. Phenol and *p*-isopropylphenol are formed in roughly the same quantities. At temperatures higher than 390 °C there seems to be a cleavage of *p*-isopropylphenol resulting in lower yields. At 340 °C the yield of phthalic anhydride reaches its maximum of 16 wt%. This means that 70% of the phthalic anhydride incorporated in the polymer can be recovered. At higher temperatures higher amounts of the fragmentation products benzoic acid and benzene are formed.

With the described method Braun et al. tried to liquefy a raw material for circuit boards covered with copper foil on both sides and reinforced with 59.5% glass fiber mats. This material was cut into pieces of 1 cm × 5 cm, so it could be put into the autoclave. The soluble yield of the resin versus the degradation temperature is shown in Fig. 32. At 340 °C the resin could be liquefied with a conversion of more than 99 wt%. It can be seen that it is not necessary to grind this material before hydrogenolysis. After cleaning with tetrahydrofuran the glass fiber mats and the copper foil were recovered with very little contamination (Fig. 33). They also tried to liquefy a variety of other thermosets using the hydrogenolysis with tetraline at 410 °C and 5 h. The results are shown in Table 21. The yield of 122% for the technical phenolic resin can be explained by the
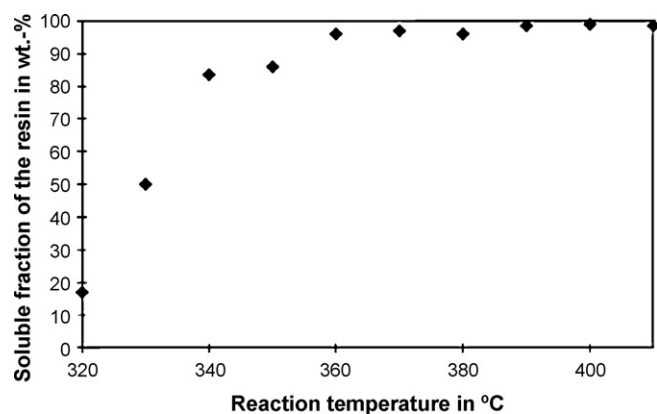
Fig. 31. Liquefied yield from epoxy resin crosslinked with phthalic anhydride versus reaction temperature by hydrogenolytic degradation [73].
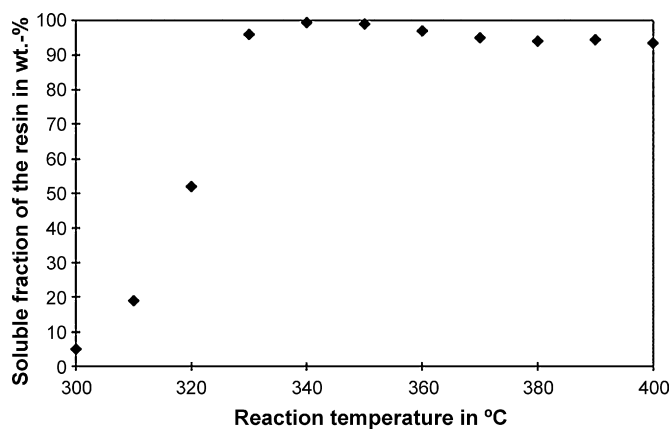
Fig. 32. Soluble yield of a raw material for circuit boards versus the degradation temperature by hydrogenolytic degradation [73].
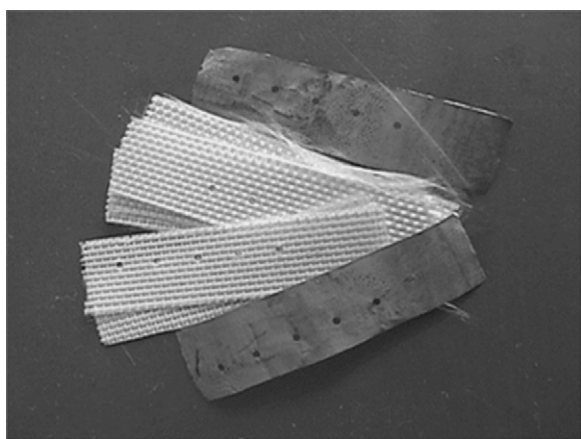

Fig. 33. Copper foil and glass fiber mats recovered from a circuit board raw material [73].

partial degradation of wood flour used as the filler material. It can be seen that this method works for all thermosets listed in the table. It could be shown that the hydrogenolysis with hydrogen donors such as tetraline and 9,10-dihydroanthracene at a temperature of 340 °C can be successfully used as a method of feedstock recycling for epoxy resins. The major degradation products like bisphenol A, *p*-isopropylphenol, phenol, phthalic anhydride and naphthaline or anthracene as the dehydrogenated donor were identified and quantitatively analyzed by gas chromatography. When adding an amine such as ethanolamine to the reaction mixture, crosslinked epoxy resins can be liquefied at 280 °C in 24 h. In their study, the hydrogenolysis was successfully applied to a variety of other ther-

mosets such as phenolic resins, melamine resins and crosslinked unsaturated polyester.

4.5. Perspectives on chemical recycling of the NMFs from waste PCBs

Generally speaking, there are four ways to recycle the NMFs by chemical methods, which are pyrolysis, gasification, supercritical fluid depolymerization and hydrogenolytic degradation. The main purpose of chemical recycling methods is to convert the polymers contained in the NMFs to chemical feedstocks or fuels. Compared with physical recycling methods, chemical recycling methods have the advantages in converting BFRs to monomers and in taking out the heavy metals left in residue. It is possible to prevent the formation of PBDD/F with optimal processing and by adding CaO in pyrolysis of the waste PCBs. The oils produced in recycling the NMFs by chemical methods should be refined before practical usage, but the cost may be higher than the conventional routes to prepare petrochemical oils and thus it might be difficult to persuade petrochemical companies to gauge their interest in the process. However, chemical recycling of the NMFs is the most effective method to take full advantage of all the elements and to remove all of the hazardous and toxic components contained in the NMFs.

The study on comprehensive processing for chemical recycling of the NMFs, taking staged-gasification for example which comprises pyrolysis and high-temperature gasification, should be brought to the forefront in order to combine the feedstock recycling with hazardous substances removing and pollution elimination. Unfortunately, such studies are limited and relatively few in available data. Therefore, the trend in chemical recycling of the NMFs from waste PCBs is to make the best of advantages over physical recycling of the NMFs to compensate the higher cost of chemical recycling methods.

5. Analysis and treatment of hazardous substances contained in non-metallic fractions from waste PCBs

Analysis and treatment of hazardous substances contained in the NMFs are important for the recycling of the NMFs from waste PCBs. However, the relevant researches are few and not systemic, most of which are on the BFRs and heavy metals in waste PCBs. Nevertheless, it is necessary to give a general review on the methods to analyze and treat the hazardous substances contained in the NMFs from waste PCBs.

5.1. Analysis of hazardous substances contained in non-metallic fractions from waste PCBs

It is included in the analysis of hazardous substances contained in non-metallic fractions from waste PCBs to determine the kinds

Table 21
Liquefied yield of various crosslinked polymers.[a].

Resin	Fillers	Yield referring to the quantity of resin (%)
Phenolic resin	40% Wood flour	122
	15% Chalk	
Melamine-formaldehyde-resin	25% Cellulose	95
	21% Chalk	
Melamine-phenol-formaldehyde-resin	30% Cellulose	98
	16% Chalk	
Epoxy resin	55% Chalk	74
	10% Glass-fiber	
Epoxy resin	50% Glass-fiber	91
	15% Kaolin	
Unsaturated polyester crosslinked with styrene	None	>99%
Polystyrene crosslinked with divinylbenzene	None	>99%

[a] Hydrogen donor: Tetraline; Temperature: 410 °C; Reaction time: 5 h [73].

and contents, toxicities and environmental impacts, fate and substance flow and leaching characteristics of hazardous substances. The hazardous substances contained in the NMFs are mainly BFRs (tetrabrombisphenyl-A (TBBA), etc.) and heavy metals (lead, beryllium, mercury, cadmium, etc.). What cannot be ignored is that PBDD/Fs can also be generated in the thermal process during the recycling course of waste PCBs. In a study entitled "Formation of PBDD/F from flame-retarded plastic materials under thermal stress", Ebert and Bahadir found out that even during the production and recycling processes of flame-retarded plastics, PBDD/F can be found in considerable amounts [74].

Environmental impacts and use of BFRs in EEE have been reviewed by Sunil [75]. BFRs are the group of brominated organic substances that inhibit the ignition of combustible materials and are commonly used in the manufacture of EEE to reduce the flammability of the product. BFRs are manufactured synthetically and following are the major classes:

(1). TBBPA: Tetrabromobisphenol-A;
(2). HBCD: Hexabromocyclododecane;
(3). PBDEs: Polybrominated diphenyl ethers consisting of Deca-BDE (Decabromodiphenyl ether), Octa-BDE (Octabromodiphenyl ether) and Penta-BDE (Pentabromodiphenyl ether);
(4). PBB: Polybrominated biphenyls.

The BFR group TBBPA represents a half of BFR volumes and is contained in 96% of PCBs. About 90% of the TBBPA produced is used as a reactive (chemically bound) flame retardant in epoxy and polycarbonate resins. Schlummer et al. analyzed the flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC–UV/MS and GPC–HPLC–UV [76]. Atmospheric pressure chemical ionisation spectra of 15 brominated and phosphate-based flame retardants were recorded and interpreted. The method was applied to detect flame retardant additives in polymer extracts obtained from pressurized liquid extraction of solid polymers.

Morf et al. have analyzed the substance flows of BFRs in recycling course of WEEE [77]. The knowledge of anthropogenic substance flows and stocks is essential for early recognition of environmental impacts and effective chemicals management. In their paper, actual levels of penta-, octa-, and decaBDE, TBBPA, and HBCD in WEEE as a major carrier of BFRs were studied. A substance flow analysis (SFA) technique has been used to characterize the flows of target substances in the recycling process from the bulk WEEE input into the output products. Average concentrations in small size WEEE, representing the relevant electric and electronic appliances in WEEE, sampled in 2003 amounted to 34 mg/kg for pentaBDE, 530 mg/kg for octaBDE, 510 mg/kg for decaBDE, 1420 mg/kg for TBBPA (as an additive), 17 mg/kg for HBCD, 5500 mg/kg for bromine, and 1700 mg/kg for antimony. In comparison to data that have been calculated by SFA for Switzerland from literature for the 1990s, these measured concentrations in small size WEEE were seven times higher for pentaBDE, unexpectedly about 50% lower for decaBDE, and agreed fairly well for TBBPA (as an additive) and octaBDE. Roughly 60% of the total bromine input determined by SFA based on X-ray fluorescence analysis of the output materials of the recycling plant cannot be assigned to the selected BFRs. This is an indication for the presence of other brominated substances as substitutes for PBDEs in electrical and electronic equipment. The presence of BFRs, in particular PBDEs in the low grams per kilogram concentration range, in the fine dust fraction recovered in the off-gas purification system of the recycling plant reveals a high potential for BFR emissions from WEEE management and point out the importance for environmentally sound recycling and disposal technologies for BFRs containing residues. Chien et al. investigated the fate of bromine in pyrolysis of waste PCBs [78]. Approximately 72.3% of total Br in the printed circuit board waste was found in product gas mainly as HBr and bromobenzene.

Heavy metals can be detected in the NMFs by using the methods which have been presented in the study by Scharnhorst et al. [79]. In their study, samples of identical PCBs have been thermally treated in a Quartz Tube Reactor (QTR) in order to detect the volatility of selected heavy metals contained in electronic scrap being of environmental concern. In preparation, evaporation experiments were performed using a thermo gravimeter (TG) in connection with an inductively coupled plasma–optical emissions spectrometer (ICP–OES). The QTR experiments were performed under reducing and under oxidizing conditions at 550 °C and 880 °C. The volatilisation has been determined for As, Cd, Ni, Ga, Pb, and Sb using ICP–OES analysis of the ash residues. The results were evaluated by thermodynamic equilibrium calculations, the TG–ICP measurements and in comparison with similar studies.

Leachability of heavy metals contained in the NMFs can be measured by using the methods as Townsend et al. presented in the study of leachability of printed wire boards containing leaded and lead-free solder [80]. The toxicity characteristic leaching procedure (TCLP) is the US EPA method used to determine a solid waste's status as a hazardous waste due to the toxicity characteristic (TC). To determine the potential waste management impacts of the alternative solders versus the tin/lead solder, two leaching tests on PCBs manufactured with five alternative types of solder were performed: the TCLP and the synthetic precipitation leaching procedure (SPLP). These tests are commonly used in the US regulatory community to assess pollutant leachability in different disposal scenarios. The TCLP and SPLP each require a 100-g sample size and liquid-to-solid ratio was 20:1. The TCLP extraction solution was prepared by diluting a mixture of 11.4 ml of glacial acetic acid (CH_3COOH) and 128.6 ml of 1 N sodium hydroxide (NaOH) to 2 l using reagent water. The final pH of the solution was 4.93 ± 0.05. The SPLP stock leaching solution was prepared by mixing 60 g of sulfuric acid with 40 g of nitric acid. This concentrated stock solution between 0.4 and 0.5 ml was placed in a 2-l volumetric flask and diluted to volume with reagent water. The resultant pH was 4.20 ± 0.05. Then 100 g of size reduced PCBs ($\leq$0.95 cm) and 2 l of leaching solution were added to each 2.2-l extraction vessel. The samples were rotated end over end at 3072 rpm for 1872 h in a 12-vessel rotary extractor (Analytical Testing Corporation). After rotation, the leachates were filtered through glass fiber filters (0.7-mm pore size) using pressure filtration and preserved by adding concentrated nitric acid until the pH of the filtrate was below 2. All the leaching tests were carried out in duplicate. The leachate samples were digested using a hot-plate acid digestion procedure (Method 3010A, EPA, 2003b). The digested samples were then analyzed for copper, lead, silver, and tin following Method 6010B (Inductively Coupled Plasma-Atomic Emissions Spectrometry) on a Thermo Terrell Ash Trace Analyzer ICP (EPA, 2003b). This instrument was not, however, equipped to analyze for bismuth. Thus, the digestates were analyzed a second time using flame atomic absorption (FLAA) spectrometry using a Perkin-Elmer 5100 Atomic Absorption Spectrophotometer. While the detection limits for each element were below the Resource Conservation and Recovery Act (RCRA) toxicity characteristic concentration limit, many of the initial results were below the detection limit, even for samples where the elements were known to be a part of the solder. Thus, many of the samples were redigested (Method 3020, EPA, 2003b) using a more sensitive technique and analyzed on the Perkin-Elmer 5100 Atomic Absorption Spectrophotometer. Laboratory blanks, sample spikes, duplicates, and calibration check samples were performed as appropriate.

The environmental safety of the products made from recycled NMFs from waste PCBs can be evaluated by using the methods which is presented by Niu and Li [58] and Shen et al. [38]. The

TCLP and SPLP methods used in the evaluation actually have already illustrated in the former paragraph. The concentration of Cu and Br leached from the PP composites reinforced with the NMFs is tested by ICP-AES according to GB 5086.1-1997 (national standards of the People's Republic of China) for solid in the study carried out Shen et al. [38].

5.2. Treatment of hazardous substances contained in non-metallic fractions from waste PCBs

Removing and treating BFRs and heavy metals from the NMFs is an ultimate method to eliminate the pollution caused by the hazardous substances. However, the research on this topic is just in its infancy and the challenges caused by technical and economic feasibility should not be underestimated. To get a clean separation between the metallic and non-metallic components from waste PCBs is a way to reduce the contents of heavy metals in the NMFs and thus a way to reduce the potential environmental risk for the recycling of the NMFs. This is not an ultimate method to eliminate the pollution caused by the hazardous substances but is a practical method to reduce the difficulty in recycling of the NMFs from waste PCBs. In fact, it is much easier and more economical to recycle the heavy metals in the MFs than to extract the residual heavy metals from the NMFs. The recycling methods of the MFs have been well reviewed by Cui and Zhang [81].

At present, the extraction of flame retardants and bromine recovery seem to be a way to treat hazardous substances contained in the NMFs from WEEE and to eliminate the pollution caused by the formation of PBDD/Fs. Altwaiq et al. have investigated the supercritical fluid extraction (SFE) using supercritical carbon dioxide (sc-CO_2) to separate additive BFRs from waste polymers [82]. Different procedures were examined to extract pure and high concentrations of a series of brominated flame retardants from various polymer materials. These procedures include supercritical carbon dioxide (sc-CO_2), modified sc-CO_2, solvent and soxhlet extraction. Extraction with sc-CO_2 gave low extraction efficiencies (between 6 and 20%) probably due to the low pressure of sc-CO_2 used. The use of toluene, acetonitrile and THF as modifier in sc-CO_2 raised the extraction efficiencies for many flame retardants. High extraction efficiencies were achieved for tetrabromobisphenol A (TBBPA), TBBPA-bis-(2,3-dibromopropylether) (TBBPA-dbp), TBBPA-carbonatoligomer (TBBPA-co) and decabromodiphenylether (DECA) (between 93 and 100%) by using 1-propanol as solvent during soxhlet extraction. Toluene instead of 1-propanol was used where insufficient extraction of the flame retardant occurred. The materials (before and after extraction) were analysed with energy dispersive X-ray fluorescence analysis (EDXRF), high-performance liquid chromatography with ultraviolet detection (HPLC–UV), gas chromatography/mass spectrometry (GC–MS) and infrared spectroscopy (IR) techniques. The properties of the extracted flame retardants such as TBBPA, TBBPA-dbp and 1,2-bis(tribromophenoxy)-ethane (TBPE) are in good agreement with those of standard reference materials. Wang et al. also studied the SFE using sc-CO_2, in whose study an additive flame retardant triphenyl phosphate ($TPPO_4$) was extracted from PCBs [83]. However, the flame retardants contained in waste PCBs are usually reactive ones, which cannot be extracted before the degradation of the thermosetting resins. As presented in the Section 4.3 of recycling the NMFs from waste PCBs by depolymerization process using supercritical fluids, the thermosetting resins contained in the NMFs can be depolymerized in supercritical water, supercritical methanol or supercritical ammonia. If a novel technology, in which depolymerization process can be coupled with the extraction process or the two processes can be completed at the same time in a certain supercritical fluid or two supercritical fluid mixtures, will be developed, the extraction and recycling of addi-
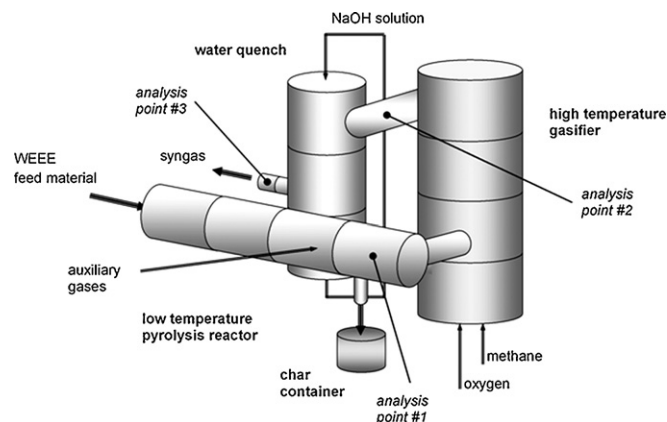

Fig. 34. Impression of the 'Pyromaat' with the material flows, gas flows, and analysis points indicated [84].

tive flame retardants contained in the NMFs from waste PCBs can be achieved.

Boerrigter et al. have studied bromine recovery from the plastics fraction of WEEE [84], which points out a potential method to recycle the BFRs contained in the NMFs from waste PCBs. The plastics fraction of WEEE containing BFRs could potentially be processed to close the bromine loop at the End-of-Life. Staged-gasification, comprising pyrolysis (550 °C) and high-temperature gasification (>1230 °C), is a process suitable for this purpose. In test runs with two plastics WEEE fraction in the ECN installation 'Pyromaat' (Fig. 34.) bromine was recovered by 'wet' alkaline scrubbing of the syngas. Utilising auxiliary gases resulted in higher percentages of volatised bromine (of >96%, compared to 81% without auxiliary gases). The produced scrubber solutions are free of contaminating organic compounds ('tars') and may contain ~95% of the bromine in the feed.

Vasile et al. studied the upgrading of pyrolysis oil from plastics and thermosets fractions of used computers [85,86]. Most of hazardous toxic compounds in liquids were eliminated after hydrogenation (e.g., halogens were removed mainly by converting them into gaseous hydrogen chloride and bromide). It has been established that the hydrogenation led to elimination of the most of hazardous toxic compounds, mainly those containing bromine. In their study, the hydrogenation catalysts were powdered commercially available DHC-8 and a metal-loaded activated carbon (M-Ac). M-Ac catalyst was prepared by wet impregnation method using metal salts. Activated carbon used as catalyst support was obtained from pyrolytic carbon black from pyrolysis at 800 °C of used scrap truck tires. The demineralized pyrolytic carbon black was activated with carbon dioxide at a flow rate of 350 ml/min for 6 h at 900 °C and then loaded with metal by impregnation method. Upgrading reactions with or without catalysts were carried out by using a 100 ml shaking type batch autoclave. The autoclave was charged with 15 g of feed and 3 g of catalyst. The autoclave was sealed and purged with nitrogen. Thereafter it was pressurized to 6.5 MPa with hydrogen. Hydrogenation runs were made at 350 °C for a reaction time of 120 min. The reaction time, temperature range and the ratio of catalyst to feed were optimized from the data of preliminary studies. Before each hydrogenation experiment the catalyst was regenerated by heating in oxygen atmosphere for 6 h. It was found that an important amount of heteroatoms in pyrolysis oils were concentrated in solid residue after hydrotreating (approximate values: Br: 5–15 wt%, C: 2–6 wt%, N: 2–4 wt%, S: 0.2–1 wt%). The most part of the oxygen-containing compounds are converted in aromatic hydrocarbons after hydrogenation while the hazardous compounds containing oxygen, nitrogen, halogens and sulphur have been eliminated. Therefore, catalytic hydrogenation can be

an effective method to eliminate the most of hazardous toxic compounds in the oil produced by chemical recycling of the NMFs from waste PCBs.

6. Conclusions

It is the NMFs that have to be recycled from waste PCBs environmental soundly. Combustion of the NMFs in municipal solid waste (MSW) will cause the formation of highly toxic PBDD/Fs while land filling of the NMFs will lead to secondary pollution caused by heavy metals and BFRs leaching to the groundwater. At present, there are generally two types of recycling methods for the NMFs from waste PCBs, which are physical recycling methods and chemical ones. One of the main considerations in physical recycling of the NMFs from waste PCBs is how to use the NMFs as effective and safe filler for different thermosetting and thermoplastic resins matrix composites. Construction materials such as concrete are another application for physical recycling of the NMFs. Adhesives, asphalts and other viscoelastic materials can be modified with the NMFs due to the composition effect. The advantages of physical recycling methods are that the processing is relatively simple, convenient, and environmental sound, the equipment invests and energy cost is low and the potential application of products made from the recycled NMFs is diversified. The main purpose of chemical recycling methods is to convert the polymers contained in the NMFs to chemical feedstocks or fuels. Included in chemical recycling methods, pyrolysis, gasification, supercritical fluids depolymerization and hydrogenolytic degradation are four ways to recycle the NMFs from waste PCBs. Compared with physical ones, chemical recycling methods have the advantages in converting BFRs to monomers and in taking out the heavy metals left in residue. It is possible to prevent the formation of PBDD/F with optimal processing and by adding CaO in pyrolysis of the waste PCBs.

The NMFs consist of cured thermosetting resins, glass fiber (cellulose paper), ceramics, BFRs, residual metals and other additives. The hazardous substances contained in the NMFs are mainly BFRs (tetrabrombisphenyl-A (TBBA), etc.) and heavy metals (lead, chromium, mercury, cadmium, etc.). What cannot be ignored is that PBDD/Fs can also be generated in the thermal process during the recycling course of waste PCBs. The toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) can be used to determine the toxicity characteristic (TC) of the NMFs and to evaluate the environmental safety of products made from the recycled NMFs.

Physical recycling of the NMFs is a promising recycling method without environmental pollution and with reasonable equipment invests and low energy cost. More work should be done to develop comprehensive and industrialized usage of the NMFs recycled by physical methods. The trend in chemical recycling of the NMFs from waste PCBs is to make the best of advantages over physical recycling of the NMFs to compensate the higher cost of chemical recycling methods. Removing and treating hazardous substances contained in the NMFs is an ultimate method to eliminate the pollution. However, the research on this topic is just in its infancy and the challenges caused by technical and economic feasibility should not be underestimated. To get a clean separation between the MFs and the NMFs from waste PCBs is a way to reduce the contents of heavy metals in the NMFs and thus a way to reduce the potential environmental risk for the recycling of the NMFs. At present, the extraction of flame retardants and bromine recovery seem to be a way to treat hazardous substances contained in the NMFs from WEEE and to eliminate the pollution caused by the formation of PBDD/Fs. However, the flame retardants contained in waste PCBs are usually reactive ones, which cannot be extracted before the degradation of the thermosetting resins. Catalytic hydrogenation can be an effective method to eliminate the most of hazardous toxic compounds in the oil produced by chemical recycling of the NMFs from waste PCBs.

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