Structural, thermal, morphological and dynamic mechanical characteristics of waste-reinforced polypropylene composites: A novel approach for recycling electronic waste

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ABSTRACT: An in-depth investigation has been carried toward utilizing polymer-rich nonmetallic fraction of printed circuit boards (PCBs) as reinforcing fillers in polypropylene (PP) composites. The influence of waste additions (up to 25 wt %) on structural, thermal, morphological, and dynamic mechanical behavior of PP composites was investigated using a range of analytical techniques. The incorporation of PCB waste was found to affect the crystalline morphology resulting in the formation of smaller spherulites. The presence of glass fibers in PCB waste promoted the formation of β-crystal enhancing the mechanical properties of composites. Thermal analysis showed a maximum increase of ~15 °C in the crystallization onset temperature (T_{co}) suggesting the nucleating effect of the filler, a feature also supported by structural investigations. Polarized microscopy revealed a reduction in the spherulite size after 5 wt % PCB waste loading owing to the presence of large number of nucleation sites. The incorporation of waste also increased the thermal stability of composites increasing the final degradation temperature by up to 14 °C. Dynamic mechanical properties of PP/PCB waste composites were determined in the temperature range −20 to 155 °C; a significant increase in the storage modulus further confirmed the reinforcing effect of waste additives. This investigation has shown that the nonmetallic fraction of PCB waste could be used as a cost-effective reinforcing filler for PP, providing an environmental friendly route to utilize electronic waste in value-added products. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43389.

INTRODUCTION

Electronic waste (e-waste) is currently among some of the fastest growing solid waste streams around the world.[1] Rapid uptake of information technology and intense marketing has resulted in the early obsolescence of many electronic devices such as mobile phones and computers. With high consumer demand, the electronics industry worldwide is now worth ~$1 trillion annually, yielding ~30–50 million tonnes of obsolete equipment each year.[2,3] Key challenges facing the recycling of e-waste are complexity due to the simultaneous presence of metals, plastics, ceramics, hazardous components and the generation of harmful emissions during processing.[4–6] Recycling is presently limited to levels around 10%, generally focused on recovering small quantities of precious/and other metals from e-waste, using approaches that may produce significant amounts of secondary waste.

Regulators in the European Union (EU) and United States (US) are working seriously toward managing the growing volumes of e-waste generated in their respective jurisdictions. However, owing to the inadequacies of the current infrastructure for reuse and recycling obsolete electronic equipment, a significant proportion of the waste generated is not managed appropriately. The overall situation is much worse in developing and transient economies such as Africa, the Indian subcontinent and China. In addition to the locally generated waste, these are further impacted by the large volumes of trans-boundary e-waste coming under the guise of second-hand/used electronic equipment. Most of the recycling in these countries is carried out in sub-standard facilities with inadequate safeguards. While high-value metals present in e-waste are generally reclaimed and recovered, most of the plastics are either burnt or trashed. Total volumes of informally and often illegally recycled electronics are not

known accurately. There is an urgent need for developing environmentally sustainable approaches for managing e-waste.

In this article, we focus our attention on the polymer-rich non-metallic fraction of e-waste that may contain up to 25–30 wt % plastics.[7] A brief overview of previous studies in this field is provided next. Over the last several years, the infrastructure for collecting and recycling electronics has grown dramatically, mostly in Europe, the United States, Japan, Korea and Taiwan. Increasingly automated technologies for harvesting metals and plastics from electronics are also being developed and deployed. Both thermosets and thermoplastics are used; there are 8–12 types of plastics commonly found in electronics.[8] Thermoset resins such as epoxy and polyamides are used in printed circuit boards (PCBs), electrical switch housing, and electrical motor components.[9] Thermoplastics have an extensive range of uses in electronic equipment, such as in frames, keyboards, connectors, and other components in electronic equipment.[10] Most commonly used plastics in electronics are as follows: high-impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) and polycarbonate (PC). In TVs, HIPS, ABS, poly(phenylene ether) (PPE), poly(vinyl chloride) (PVC) and PC can be found, whereas polyphenylene oxide (PPO) and PC/ABS blends are present in computers.[8,11] Given the volumes of wastes being generated, there is an urgent need for developing additional/alternative routes for their utilization in value-added products.

E-waste polymers are currently recycled through mechanical, thermal, and chemical processes. Mechanical processing consists of the separation of different types of polymers, identification by turbo-electric separation followed by size reduction to give uniformity to particles. To remove other materials, processes such as magnetic separation, eddy current processing and air classification have been carried out.[12,13] Chemical processes use end-of-life plastics as a feedstock for petrochemical processes, such as in coal-making or as a reducing agent in smelting processes, such as steel making, which use hydrocarbon sources to reduce metal oxides.[14] Plastics can also be utilized in the form of energy through thermal recycling. These have high calorific value, so release energy in the form of heat upon combustion.[15] Nonmetallic PCB waste has also been evaluated as filler in polypropylene (PP) and investigated the effect of filler on tensile, flexural and fracture behavior.[16–20]

In this article, we report an in-depth investigation on the utilization of the polymer-rich nonmetallic fraction of waste PCBs in PP-based composites. The focus in this study is to develop a fundamental understanding of the effect of PCB waste on structural, thermal, morphological, and mechanical properties of reinforced PP composites. A large number of measurements were carried out on these composites in order to determine the influence of waste PCB additives. By replacing expensive fillers/polymers in thermoplastic composites, this novel recycling approach is expected to enhance the utilization of electronic waste in a cost-effective and environmentally sustainable manner.

EXPERIMENTAL

Materials
Polypropylene REPOL H110MA, an injection molding grade plastic with a density of 0.91 g/cm^3 and a melt flow index of

Table I. ICP-OES Results of PCB Waste Powder

Elements (major)	Al	Cu	Fe	Pb	Sn	
Quantity (wt %)	2.450	2.096	2.019	0.285	0.635	
Elements (minor)	Au	Mg	Ni	Pd	Pt	Zn
Quantity (ppm)	116	1399	680	4	6	2073

11 g/10 min at 230 °C, was used in this investigation. The PCB waste powder was prepared by crushing several scrap motherboards obtained from personal computers (PCs); the metal-rich fraction was removed using the froth floatation method based on relative differences in densities. The lighter nonmetallic fraction (labeled hereafter as PCB waste) was used in this investigation. Optima 7300DV ICP-OES (inductively coupled plasma optical emission spectrometry) was used for the elemental analysis of PCB waste. For this purpose, the specimens were digested in aqua regia, which is a mixture of hydrochloric acid and nitric acid in the proportion of 3:1. The solution containing elements in atomic state was analyzed quantitatively by ICP-OES. This method uses plasma energy to detect trace metals by generating spectrum rays and wavelengths to identify specific elements. Plasma was generated by applying high-frequency electric current to ionize argon gas. It can produce temperatures up to 7000 K, thereby exciting a large number of elements. This technique is also capable of analyzing multiple constituents simultaneously; various metallic concentrations could be measured to an accuracy of ±1%. The results of this analysis have been summarized in Table I. The SEM/EDS images of raw PCB waste are presented in Figure 1. The main constituents of PCB waste powder were glass fibers and epoxy/phenolic resin particulates and a small residual fraction of metals and ceramics.

Preparation of PP/PCB Waste Composites by Melt Compounding
PP and PCB waste powders were dried in a vacuum oven at 70 °C for 3 h prior to mixing. PP was first mixed with PCB waste in a range of proportions (0–25 wt % PCB, the mix labeled as PP-X where X represents the concentration of PCB waste). The melt compounding of the mixture was carried out in a single-screw extruder (HAAKE) at 200 rpm; the temperature of different zones of the extruder was between 180 and 210 °C. The composite strands obtained from extrusion were pelletized by a granulator. These were dried for 3 h at 80 °C prior to injection molding. The injection molding of the composites was carried out using L&T Demag PFY-40 LNC 4P for making testing samples as shown in Figure 2. The temperatures in the injection molding machine were between 180 and 210 °C, similar to those used during extrusion. The injection pressure was kept at 50% of the maximum pressure (1766 bar) and cooling time was 25 s.

Characterization of PP/PCB Waste Composites
Wide-Angle X-ray Diffraction. Wide-angle X-ray diffraction (WAXD) analysis of the injection-molded samples was carried out using PANanalytical X'Pert PRO diffractometer (The Netherlands), model PW 3040-60 using Ni-filtered Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) at 40 kV and 40 mA. WAXD analysis was used to characterize the crystallinity and the orientation of samples along with shifts, if any, in various diffraction peaks as a function of
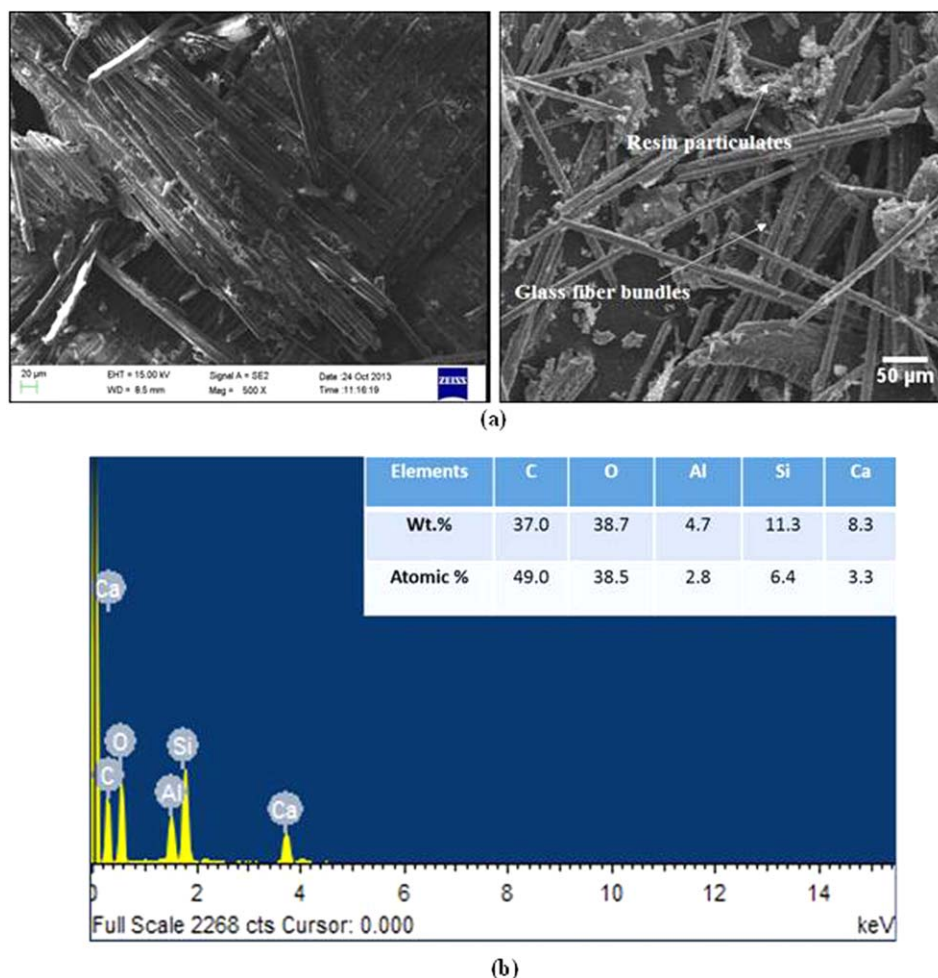
Figure 1. (a) SEM images of PCB waste powder and (b) EDX results of PCB waste powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

waste concentration. The crystallinity of samples was calculated using the peak area integration method over the angular range 5–35° (range typically used for PP), after curve fitting and the separation of amorphous and crystalline components.

Differential Scanning Calorimetry. "TA Instruments Q 200" differential scanning calorimeter (DSC) was used for recording DSC scans (heating-cooling-heating) under nitrogen atmosphere. About 5–6 mg of sample was first heated from room temperature to 190 °C at a heating rate of 10 °C/min and then held at that temperature for 5 min to remove the thermal history of the material. The sample was then cooled down to ambient temperature at the rate of 10 °C/min and heated once again to 190 °C at the same rate. Cooling scans were used for crystallization studies and second heating scans were used for investigating the melting behavior. DSC was calibrated for enthalpy and temperature using pure indium metal.

Thermogravimetric Analysis. The thermal stability of PP and PP/PCB waste composites was determined by recording thermogravimetric (TG) and derivative thermogravimetric (DTG) traces (Perkin Elmer Pyris 6 TGA) in nitrogen atmosphere. A

sample quantity of 5–6 mg and a heating rate of 20 °C/min was used in each experiment.

Morphological Characterization. For scanning electron microscope (SEM) and energy-dispersive X-ray spectrometer (EDS) investigations, samples were prepared as per the following procedure. Composites were cut and then mounted in epoxy resin in plastic molds (25 mm diameter). Surfaces were ground on six different grades of silicon carbide paper under running distilled water and polished with pads covered in diamond paste. The mounted material was then carbon or gold coated, and examined under a SEM equipped with EDS for chemical analysis and elemental mapping.

Polarized Light Microscopy Analysis. Polarized light microscope (Meizi, Japan) equipped with a hot stage was used to investigate the crystalline morphology, the size of spherulite, and spherulitic growth of PP and PP/PCB waste composites. Thin film samples of different compositions were sandwiched between two glass slides, heated up to 200 °C and maintained there for 3 min to remove thermal history. The sample was then cooled to a fixed crystallization temperature, i.e., 132 °C at the rate of 50 °C/min. PP samples were held at this temperature
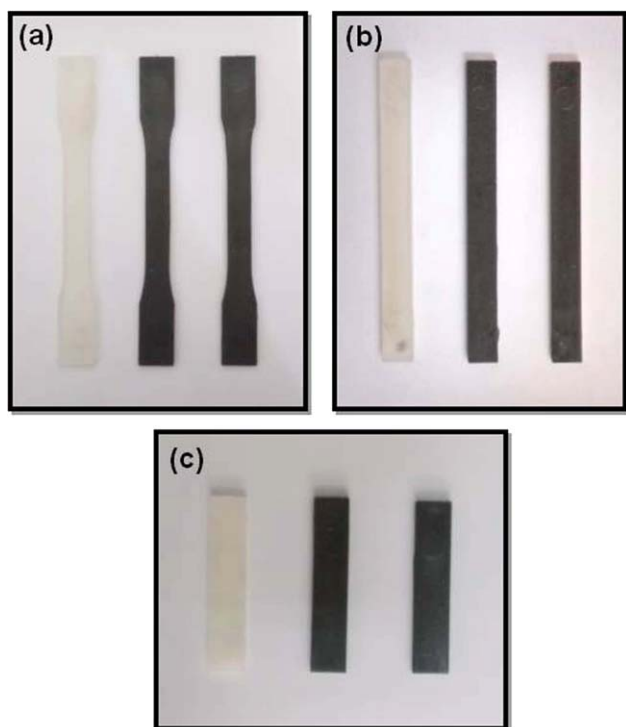
Figure 2. Samples of PP/PCB waste composites for (a) tensile, (b) flexural and (c) impact testing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(132 °C) and the crystal growth was investigated as a function of time. For all other samples, the spherulitic growth was seen at 132 °C after 5 min under isothermal conditions. The crystalline morphologies were recorded by taking images at regular time intervals with the microscope (resolution: 12 mega pixel; maximum magnification: 203).

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) measurements were carried out on composite test specimens of dimensions $17.5 \times 12.8 \times 3$ mm^3 in the flexure mode on Q800 (TA Instruments, USA) to characterize the storage modulus, loss modulus and tan δ for a quantitative determination of reinforcement effects to ascertain the shift, if any, in the glass transition temperature of composites in the temperature range of -20 to -155 °C at a frequency of 1.0 rad/s and a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

An in-depth characterization of PCB-reinforced PP composites was carried out using a range of techniques. Detailed results are presented below.

Structural Characterization
Figure 3 shows the WAXD pattern for pure PP and PCB waste-reinforced PP composites. Diffraction peaks at 2θ values of 13.9°, 16.7°, 18.4° and 21.7° respectively, correspond to (hkl) planes (110), (040), (130), (131) + (041) of the α-form of PP. The diffraction peak at 21.0° represents overlapping peaks: $\alpha(111) + \beta(301)$.[21]

According to Hermans and Weidingeer,[22] the relative crystallinity of the samples was calculated from the diffraction pattern using the following equation to normalize intensities belonging to the crystalline and amorphous components.

$$\chi_c(\%) = \frac{A_c}{A_c + A_a} \times 100, \qquad (1)$$

where A_c is the area of the crystalline region, A_a the area of the amorphous region and χ_c is the percent crystallinity. These results have been presented in Figure 4; corresponding results from DSC measurements have also been included in the figure for sake of comparison.

The WAXD results show that the incorporation of PCB waste in PP did not have much effect on the overall crystallinity of composites ($\sim$3%). The incorporation of any heterogeneous moiety in the polymer matrix is known to decrease the overall crystallinity of composites due to hindrance in crystal growth. However, in the present case, the PCB waste was seen to act as a nucleating agent for the PP matrix. This was indicated by the initiation of the peak (β phase) at $2\theta = 16°$ and also by the increase in the crystallization onset temperature with increasing waste in DSC data (Table II). There was a marginal reduction in the crystallinity of composites for up to 10 wt % waste loading as the hindrance in crystal growth of PP exceeded the nucleation effect of the filler. The crystallinity of the composites at 15 wt % PCB waste loading showed an increase with the nucleating effect by PCB waste becoming more significant. This was further confirmed by the increasing intensity of the diffraction peak at 16° (marked by "*" and "β" in Figure 3) corresponding to $\beta(300)$ crystalline form of PP.[21] This increase in crystallinity is attributed to a large number of nucleation sites for the β phase overcoming the hindrance by PCB waste in crystal growth. However, the overall crystallinity of the composites as well as β-crystal nucleation was seen to decrease slightly for higher PCB loadings. The relative decrease in the peak intensities (β-crystal) at 20 and 25 wt % PCB waste loading can also be seen in Figure 3. After 15 wt % waste loading, the peak intensity corresponding to $\beta(300)$ crystal form of PP was found to decrease showing a marginal influence of nucleation at these compositions. This reduction in crystallinity is attributed to high filler contents causing a hindrance in crystal growth along with a reduction in the nucleating effect of filler due to waste agglomeration resulting in a reduced number of nucleation sites.

Thermal Characterization
Differential Scanning Calorimetry. Figures 5 and 6 show the DSC scans of cooling and heating, respectively, for pure PP and PP/PCB waste composites. DSC cooling crystallization curves reveal that PCB waste acted as a nucleating agent for the PP matrix as the crystallization onset temperature (T_{co}) and crystallization peak temperature (T_c) of PP increased with its addition for all compositions (Table I). T_{co} and T_c were determined from DSC cooling crystallization exotherms using TA Universal Analysis software. T_{co} represents the temperature where crystallization exotherm starts and T_c the peak exotherm temperature. There was an increase of $\sim$11.2 °C in T_c for composite with 5 wt % addition of PCB waste supporting the nucleation effect
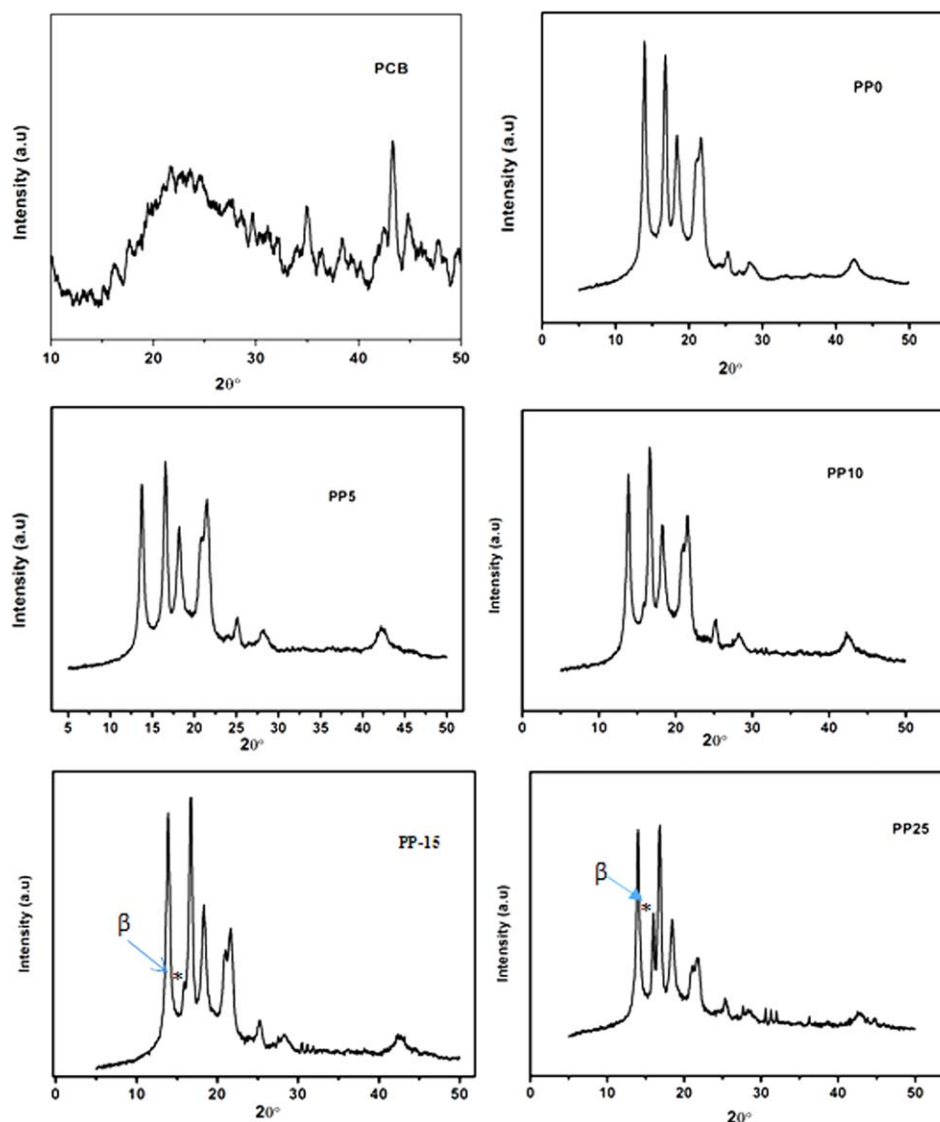
Figure 3. X-ray diffractograms of PCB, PP and PP/PCB waste composites (intensity vs. 2θ). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
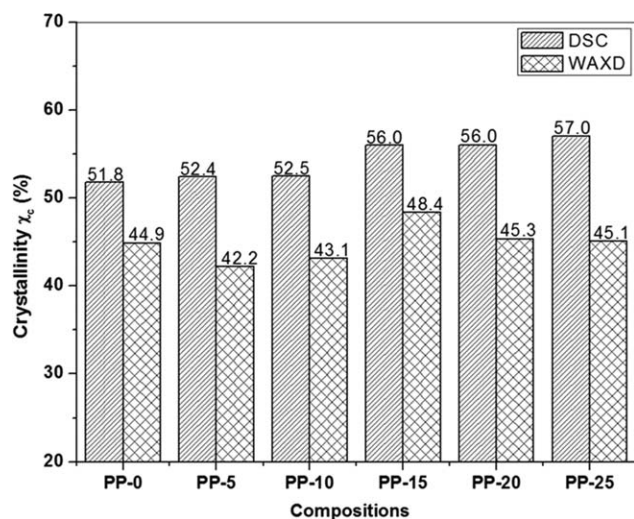

Figure 4. Crystallinity of composites as determined through WAXD and DSC analysis.

due to PCB waste. The magnitude of T_c showed an increase with increasing loadings of PCB waste and a maximum increase of ∼15 °C was observed for a loading of 20–25 wt %. This increase in the crystalline onset temperature for these composites is in good agreement with WAXD data (Figure 3) which provided clear evidence for the nucleation of the β phase. The DSC heating curves indicate that PCB waste enhanced the melting temperature of composites by about 2–3 °C as compared to pure PP. This increase in the melting temperature can be attributed to the restrictions caused by the PCB waste in the chain mobility of PP as well as to the increased crystallinity.

The crystallinity of these composites was also computed from the melting enthalpy data obtained from DSC second heating scans. From the area under the endothermic transition, the melting enthalpy (ΔH_f) was calculated for different compositions and was used to determine the normalized percent crystallinity (χ_c) using the following equation:

Table II. Results from DSC Analysis of PP/PCB Waste Composites

Sr. No.	Sample Designation	T_m (°C) (Melting)	T_{co} (°C) (Crystallization Onset)	T_c (°C) (Crystallization Peak)	ΔH_f^a (J/g)	χ_c^a (%)
1	PP-0	161.9	116.7	111.7	107.3	51.8
2	PP-5	164.0	126.3	122.9	103.0	52.4
3	PP-10	164.5	128.1	124.7	97.9	52.5
4	PP-15	164.8	127.3	123.5	98.5	56.0
5	PP-20	165.0	129.7	126.2	92.7	56.0
6	PP-25	164.7	130.0	126.7	88.5	57.0

[a] ΔH_f is melting enthalpy of the samples and χ_c is normalized percent crystallinity.

$$\chi_c(\%) = \frac{\Delta H_f}{\Delta H_{fo}(1-f)} \times 100, \tag{2}$$

where ΔH_f is the melting enthalpy of sample (J/g), ΔH_{fo} is 207 J/g, melting enthalpy for 100% crystalline PP,[23] and f is the weight fraction of the filler.

These results have been presented in Figure 4 and are compared with corresponding results from WAXD analysis. The percent crystallinity of composites obtained from DSC results showed almost no change for up to 10 wt % PCB waste and an increase of ~3–5 units at higher concentrations. The crystallinity remained fairly constant up to 25 wt %. On the whole, the percentage crystallinity as calculated from the heat of fusion showed an increase with the incorporation of PCB waste. The increase in crystallinity at 15 wt % was caused by the nucleation of β phase of PP by PCB waste as described earlier in the WAXD analysis. Although the crystallinity values from DSC data followed trends similar to XRD study, the values obtained from the DSC analysis were somewhat higher. In DSC investigations, the thermal history of the composite samples was removed and the matrix allowed to recrystallize at a controlled cooling rate resulting in an improved crystallization. On the other hand, in WAXD analysis, the injection-molded samples

were used directly for crystallinity determination and had relatively shorter cooling times for the crystallization process. This difference resulted in relatively lower crystallinity values.

Thermogravimetric Analysis. Figure 7 shows thermogravimetric plots for pure PP, 100% PCB waste and PP/PCB waste composites; the corresponding degradation temperatures at weight losses ranging from 10 to 80% have been presented in Table III. The relative thermal stability was analyzed by comparing the degradation temperature at varying mass losses (%), temperature at the maximum rate of mass loss (T_{max}), and percent char yield at 700 °C. From Figure 7, it can be seen that PCB waste showed an early degradation starting at 300 °C and a significant proportion had degraded by 400 °C; its final degradation temperature was recorded as 741 °C. This early degradation of residual PCB waste corresponds to the presence of epoxy resin which has low thermal stability.[24] Above 400 °C, the PCB waste demonstrated good thermal stability and not much degradation was observed due to the presence of chars, glass fibers and ceramics.

The incorporation of 5% PCB waste in PP composites (PP 5) reduced the overall thermal stability as both the degradation onset temperature (T_{on}) and degradation end temperature (T_{end}) registered a reduction of 35 and 12 °C respectively. However, the thermal stability of the composites was found to increase with
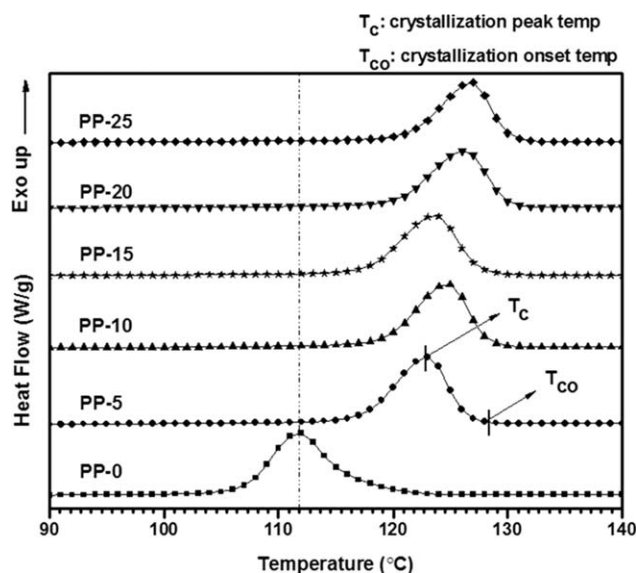
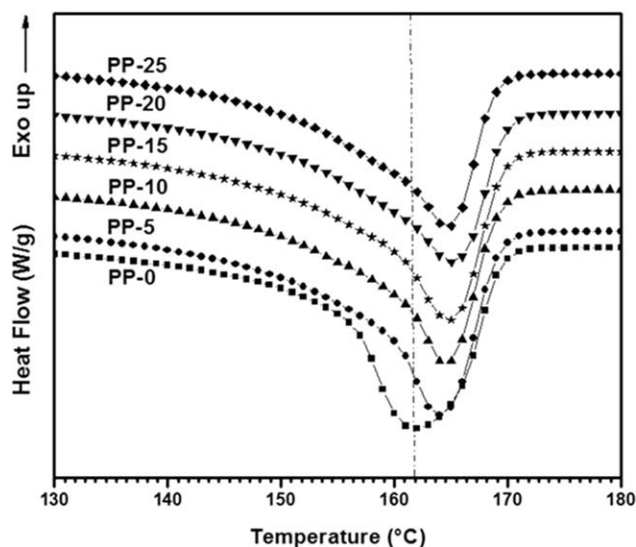**Figure 5.** DSC scans (cooling) of PP and PP/PCB waste composites.

Figure 6. DSC scans (heating) of PP and PP/PCB waste composites.
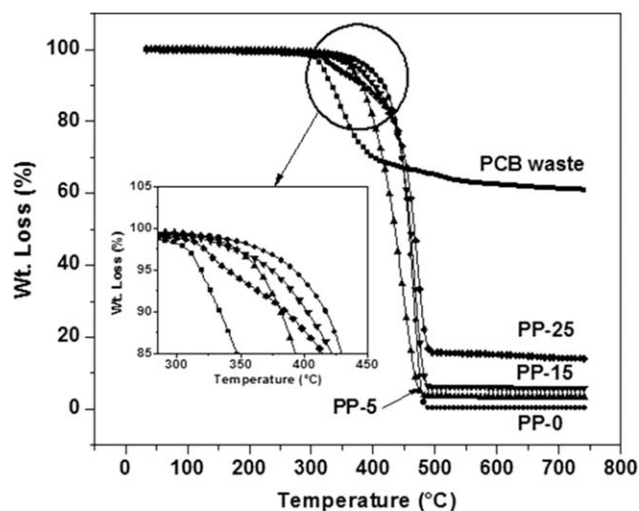
Figure 7. Thermogravimetric traces of PCB waste, PP, and PP/PCB waste composites (PP-5 and PP-25).

increasing loadings of PCB waste. A marginal drop in T_{on} at 20 and 25 wt % suggests a rapid degradation of the composite matrix due to the presence of higher amounts of thermally unstable epoxy phase at these concentrations. T_{end} of the composites showed a maximum increase of 14 °C at 25 wt % loading as compared to pure PP. The gradual increase in T_{end} with increasing PCB waste content is attributed to the high thermal stability of residual chars/glass fibers/ceramics present in the PCB waste. The thermal stability of these composites can also be represented by the percent char yield after the complete degradation of composites. Both experimental and theoretically estimated char yields at 700 °C have also been presented in Table III. There was a good agreement in the experimental char yield and char yield calculated theoretically. The percent char yields of composites increased with increasing PCB loadings; this represents enhanced thermal stability for composites with increasing filler loadings.

Microscopic Investigations. SEM/EDS results for PP-25 composites are shown in Figure 8. Back-scattered images (upper left) show silica fibers as bright spots; ceramic impurities can be seen as light gray precipitates of random shapes. Dark gray background shows the PP matrix. It can be seen clearly that silica fibers were oriented randomly in the matrix; some of these can

be seen in plane, while several of these were perpendicular to the plane of observation. These were present either as single fibers or as bundles. A high magnification SEM of fiber bundles is shown on the lower-left. The EDS analysis of these fibers (upper right) shows that while silica was the main constituent, these fibers also contained ceramic impurities such as calcium and alumina. A small impurity in the near vicinity of these fibers (lower right) was found to be composed of lead, tin, carbon and alumina.

Polarized Light Microscopy Analysis. The crystalline morphology of PP and PP/PCB waste composites was also analyzed using hot-stage polarized microscopy; the corresponding images are shown in Figures 9 and 10. Figure 9 shows the spherulite growth of PP as a function of time and Figure 10 shows the ultimate crystalline morphology in PP/PCB waste composites at different PCB waste loadings. The microscopic images for pure PP reveal the formation of spherulites which grew with time and reached their fully grown state after isothermal aging at 132 °C for 5 min. The average spherulite size was observed to be ~40 μm. With increasing concentrations of PCB waste, the shape of spherulites became distorted and the size of the spherulite became much smaller, especially after 5 wt % PCB waste loading (Figure 10). It can be seen clearly that PCB waste had a significant influence on the crystallization process of PP and its spherulitic growth. The PCB waste acted as a nucleating agent for the PP matrix giving rise to a large number of nuclei in a limited space resulting in the formation of imperfect spherulites with increasing PCB waste content. The presence of large number of nuclei centers also caused a high level of crystalline defects.[15] These results from light microscopy further corroborate the heterogeneous nucleation promoted by PCB waste as observed in DSC analysis.

Dynamic Mechanical Analysis. The dynamic mechanical analysis of PP/PCB waste composites was carried out to investigate the influence of waste additives on their storage modulus (E') and loss modulus (E'') at different temperatures. Figure 11 shows their variation as a function of temperature for a range of compositions. From Figure 11(a), the storage modulus of PP/PCB waste was seen to increase with increasing waste loading up to 15 wt %, followed by a sudden drop at 20 wt % and later an increase at 25 wt % PCB waste loading. The maximum storage modulus was observed for composites with 15 wt %

Table III. Thermogravimetric Analysis of PP, PCB Waste, and PP/PCB Waste Composites

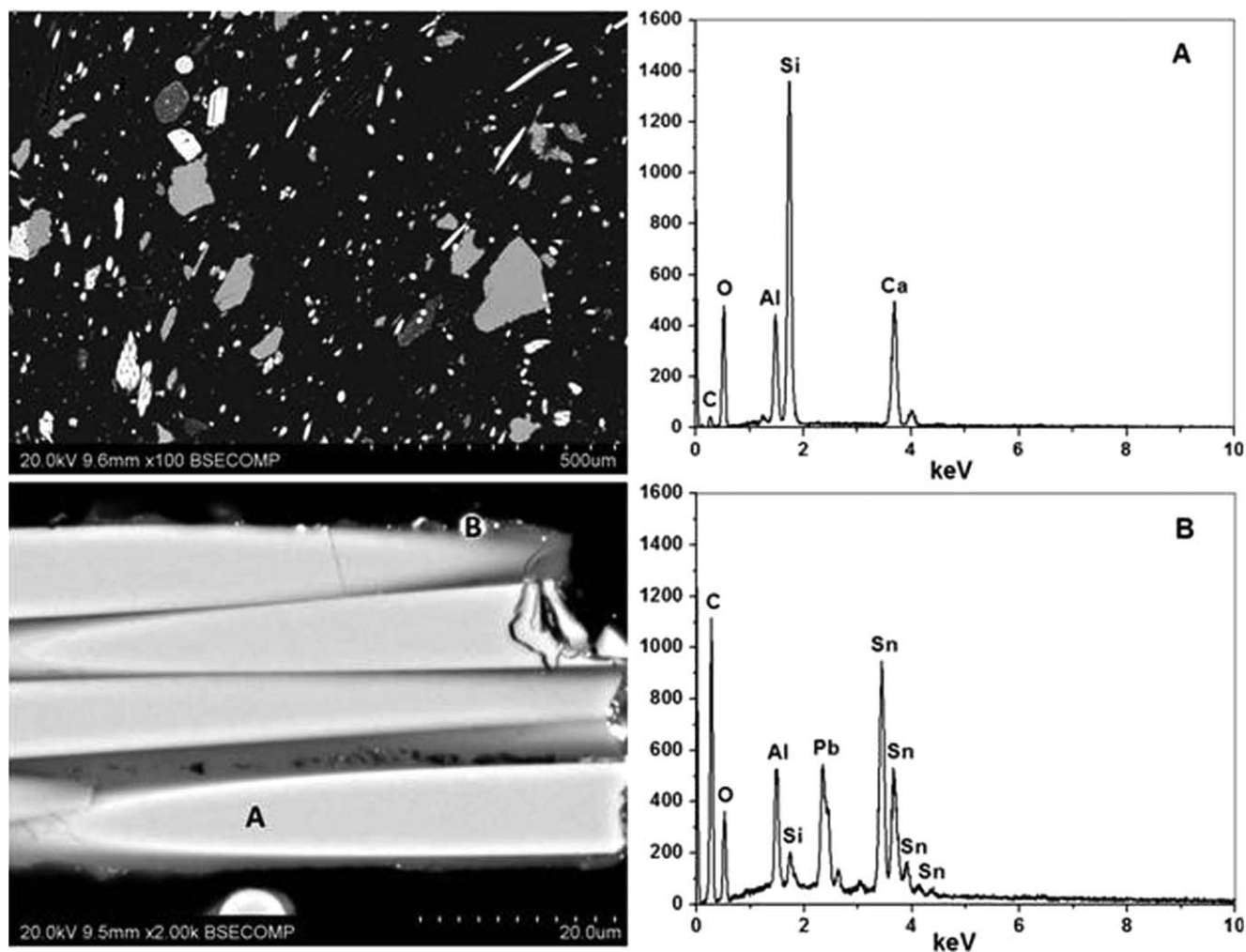| Sample Designation	Degradation Temperature (°C), at % Mass Loss			Temperature at Maximum Rate of Mass Loss (T_{max})	Char Yield (%) at 700 °C	Theoretical Char Yield (%) at 700 °C
	20	40	80			
PP-0	437	453	470	465	–	–
PP-5	401	426	458	453	3.3	3.06
PP-10	432	454	474	466	5.8	6.13
PP-15	434	455	475	467	5.9	9.20
PP-20	436	458	480	469	12.0	12.26
PP-25	434	460	484	472	15.0	15.32
PCB waste	359	741	–	352	61.3	–

Figure 8. SEM/EDS images for PP-25 composites.

PCB waste loading (PP-15); all other composites showed values intermediate between neat PP and PP-15. The increase in storage modulus for all compositions over the entire temperature range indicates PCB waste to be a good reinforcing filler for PP matrix. This waste was found to increase the stiffness of composites and allowed for a homogenous stress transfer to the matrix. With increasing waste loading, the stress was distributed more evenly resulting in an increased storage modulus. A decrease in the storage modulus value after 15 wt % PCB waste loading could be attributed to the agglomeration of PCB waste at higher loadings. The stiffening effect of PCB waste was found to be more prominent in lower temperature values as compared to higher temperature probably due to a mismatch in thermal coefficients of the PP matrix and the filler. This however allowed for a better stress transfer between the matrix and the filler at lower temperatures.[25]

Figure 11(b) shows the variation of the loss modulus with temperature for a range of compositions. Loss modulus corresponds to the viscous component of the composites and provides an indication regarding the energy dissipated in the matrix. The loss modulus of these composites was found to increase over the entire temperature range investigated. This increase points to enhanced energy absorption due to high amounts of interfacial area between PCB waste and the PP matrix; a stronger interface results in low levels of dissipation energy and a weak adhesion between PCB waste and PP.

Influence of Metallic Impurities
As per the initial characterization of waste PCB powder, a range of metallic impurities were also present in its polymer-rich component (Table I). These were present either as metals and alloys (Cu, Pb, Sn) or as ceramic oxides (Al_2O_3, Fe_2O_3, MgO, ZnO); a small amount of precious metals were present as well. Most of the results presented above on PP-PCB composites however indicate that the presence of small amounts of metallic impurities did not have much influence on the range of characteristics investigated. However, it is important to note that this may not be the case in all scenarios due to variations in the compositions of waste PCBs and their associated influence on composite characteristics. The results presented in this article represent basic trends only and provide an environmentally sustainable avenue for the utilization of e-waste in value-added products.
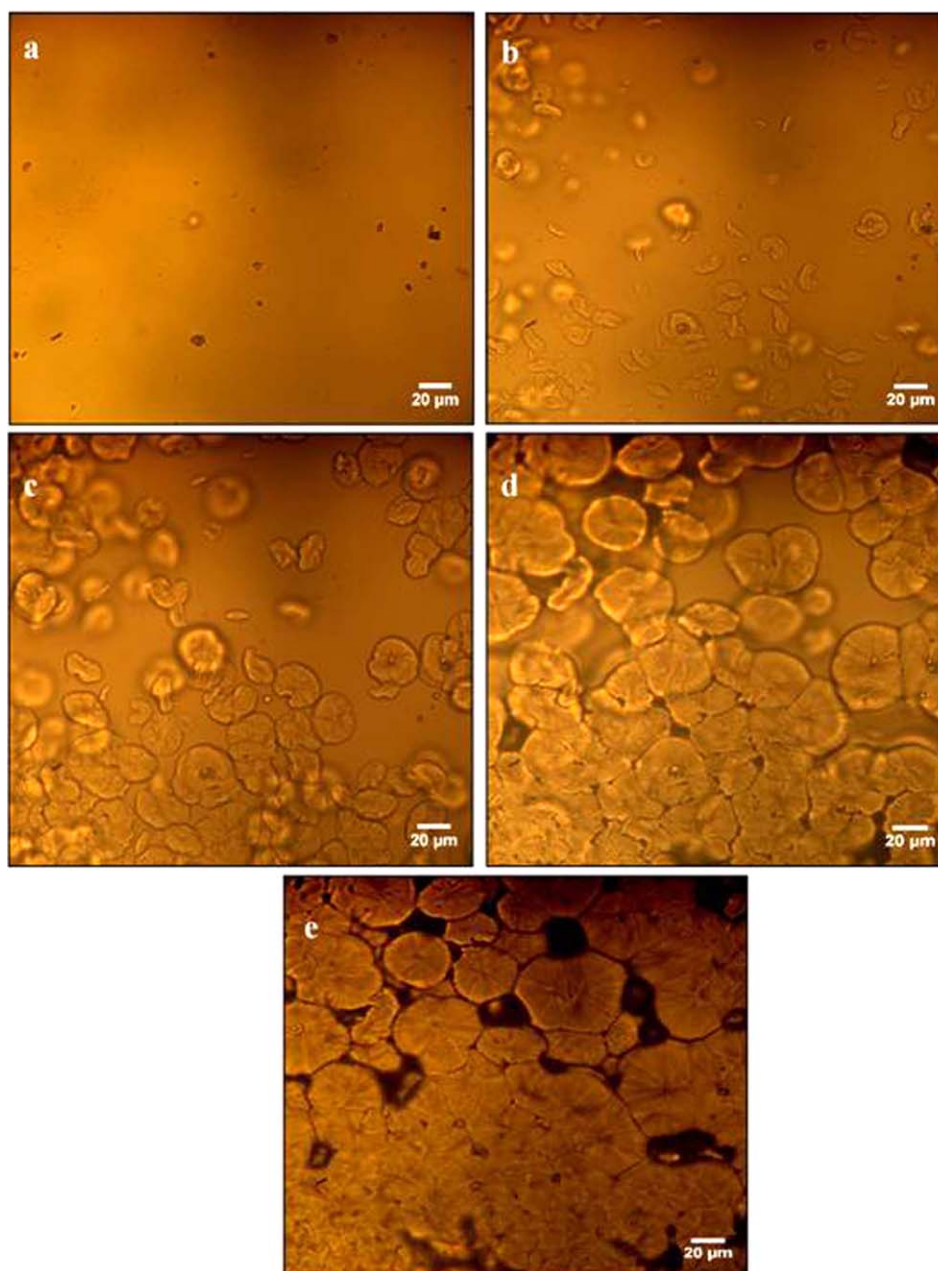
Figure 9. PLM micrographs of PP showing effect of crystallization time: (a) 0 s, (b) 75 s, (c) 150 s, (d) 225 s, and (e) 300 s at 132 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The nonmetallic fraction of PCB waste (up to 25 wt %) was used as a reinforcing filler in PP matrix and these composites were evaluated for thermal, structural, morphological and mechanical characteristics. The key conclusions from the study are:

1. The PCB waste acted as a nucleating agent as indicated by an increase in the overall crystallinity along with the initiation of a peak at $2\theta = 16°$ indicating the nucleation of $\beta(300)$ crystal form of PP.
2. The nucleating effect of PCB waste was also reflected in the DSC results as a maximum increase in crystallization onset temperature of ∼15 °C was observed at 25 wt % PCB waste loading supporting the heterogeneous nucleation by PCB waste. The crystallinity of composites was seen to increase gradually; the melting point of the composites however showed only a modest increase of ∼2–3 °C.
3. Thermogravimetric analysis showed that the addition of PCB waste enhanced the thermal stability of PP composites as indicated by an increase in T_{end}; however, a marginal reduction in the initial degradation was observed at lower waste loadings. The initial degradation below 400 °C was attributed to the presence of epoxy resin in the PCB waste powder. SEM/EDS analysis indicated the presence of small amount of metallic impurities like lead and tin in addition to glass fibers.
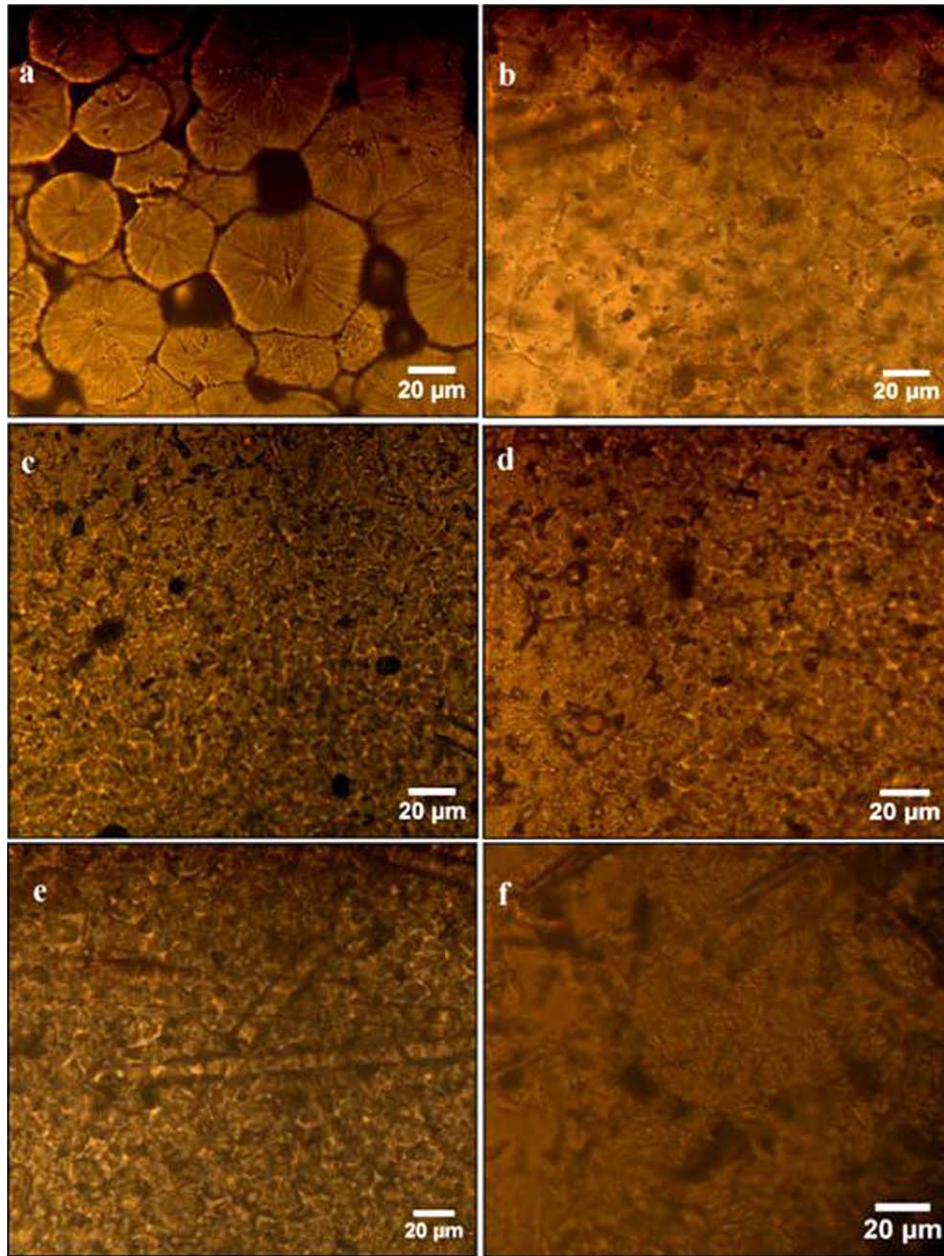
Figure 10. Final crystalline morphology of PP and PP/PCB waste composites: (a) PP-0, (b) PP-5, (c) PP-10, (d) PP-15, (e) PP-20 and (f) PP-25. [isothermal crystallisation ti,e 300s at 132 °C]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
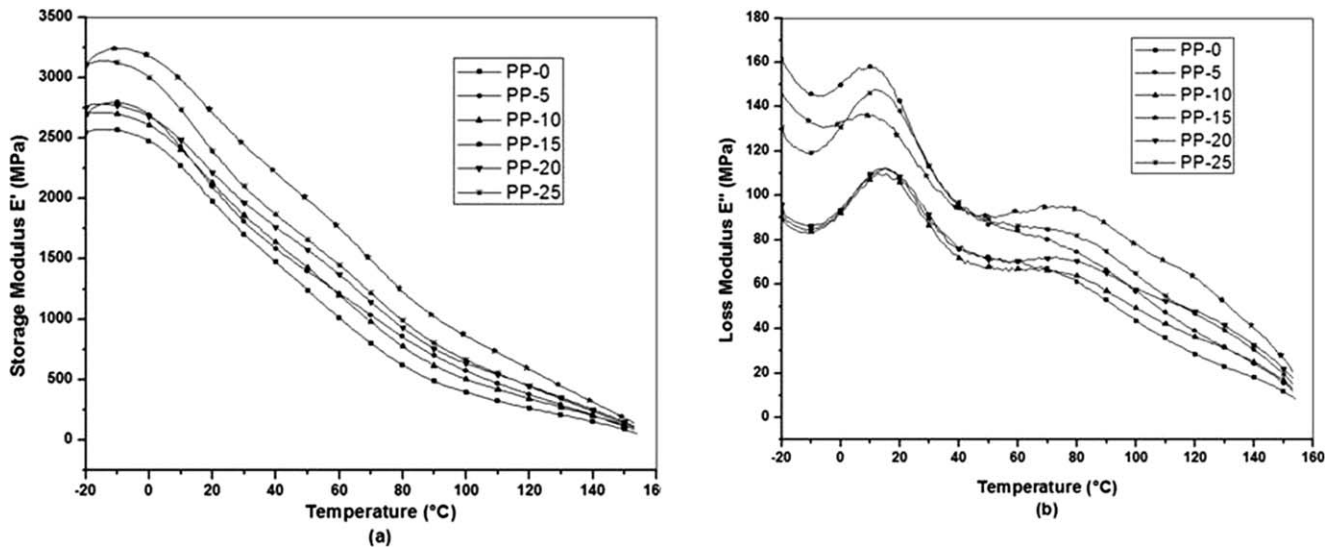

Figure 11. Dynamic mechanical analysis plots: (a) storage modulus (E') and (b) loss modulus (E'') of PP and PP/PCB waste composites as a function of temperature.

4. Polarized light microscopy analysis results showed that the spherulite size of PP/PCB waste composites decreased as compared to that of pure PP; this was attributed to the generation of large number of nucleation sites and due to the hindrance by glass fibers present in PCB waste.

5. The storage modulus value of composites was seen to increase up to 15 wt %; higher loss modulus values indicated poor interfacial adhesion between PCB waste and PP as indicated by the DMA results.

6. This in-depth investigation has shown that PCB waste could be used to replace several costly fillers for reinforcing PP. In view of growing amounts of PCB waste, the incorporation of this waste in widely used commodity plastics composites could help develop an economical approach toward recycling large amounts of waste in an environmentally sustainable manner.

REFERENCES

1. Proposal for a directive of the European parliament and of the council on waste electric and electronic equipment, European Commission, **2000**.

2. Call for global action on e-waste, United Nations Environment Programme, **2006**.

3. Gover, J. E. IEEE Piscataway: New York, **1993**, p 57.

4. Kasper, A. C.; Berselli, G. B. T.; Freitas, B. D.; Tenório, J. A. S.; Bernardes, A. M.; Veit, H. M. *Waste Manag.* **2011**, *31*, 2536.

5. Sum, E. Y. L. *J. Mater. Sci.* **1991**, *43*, 53.

6. Chancerel, P.; Meskers, C. E. M.; Hagel, C.; Rotter, V. S. *J. Ind. Ecol.* **2009**, *13*, 791.

7. Menad, N.; Bjo, B.; Allain, E. G. *Resour. Conserv. Recycl.* **1998**, *24*, 65.

8. Kang, H. Y.; Schoenung, J. M. *Resour. Conserv. Recycl.* **2005**, *45*, 368.

9. Hall, W. J.; Williams, P. T. *Resour. Conserv. Recycl.* **2007**, *51*, 691.

10. Wu, B. Y.; Chan, Y. C.; Middendorf, A.; Gu, X.; Zhong, H. W. *J. Environ. Sci.* **2008**, *20*, 1403.

11. Tarantili, P. A.; Mitsakaki, A. N.; Petoussi, M. A. *Polym. Degrad. Stab.* **2010**, *95*, 405.

12. Biddle, M.; Dinger, P.; Fisher, M. *IdentiPlast II Conference Reprint*, Brussels, 26–28 April, **1999**.

13. Stessel, R. I. In Recycling and Resource Recovery Engineering: Principles of Waste Processing, 1st ed.; Forstner, U., Murphy, R. J., Rulkens, W. H., Eds.; Springer: Berlin and Heidelberg, **1996**, p 205.

14. Xiao, C.; Biddle, M. B. and Fisher, M. M., Proceedings, SPE 6th Annual Recycling Conference ARC'99, Detroit, Michigan, November 9-11, **1999**, p 219.

15. Fisher, M. M.; Mark, F. E.; Kingsbury, T; Vehlow, J.; Yamawaki, T. In Electronics and the Environment, Proceedings of the 2005 IEEE International Symposium, New Orleans, USA, 16–19 May **2005**, p 83.

16. Huabo, D.; Jia, W.; Jinhui, L. Sustainable Systems and Technology, IEEE International Symposium held at New Orleans, USA, 18–20 May **2009**, p 1. DOI: 10.1109/ISSST.2009.5156715.

17. Zheng, Y.; Shen, Z.; Cai, C.; Ma, S.; Xing, Y. *J. Appl. Polym. Sci.* **2009**, *114*, 1856.

18. Zheng, Y.; Shen, Z.; Cai, C.; Ma, S.; Xing, Y. *J. Hazard. Mater.* **2009**, *163*, 600.

19. Marques, A. C.; Cabrera Marrero, J. M.; de Fraga Malfatti, C. *SpringerPlus* **2013**, *2*, 521.

20. Zheng, Y.; Shen, Z.; Cai, C.; Ma, S.; Xing, Y. *Mater. Des.* **2009**, *30*, 958.

21. Machado, G.; Denardin, E. L. G.; Kinast, E. J.; Gonçalves, M. C.; Luca, M. A. de.; Teixeira, S. R.; Samios, D. *Eur. Polym. J.* **2005**, *41*, 129.

22. Hermans, P. H.; Weidingeer, A. *Makromol. Chem.* **1961**, *44–46*, 98.

23. Wunderlich, B. Thermal Analysis; Academic Press: New York, USA, **1990**, p 417.

24. Zulfli, M. A.; Chow, A. B. W. S. *Malaysian Polym. J.* **2012**, *77*, 8.

25. Zhang, H.; Zhang, Z. *Eur. Polym. J.* **2007**, *43*, 3197.