

# Environmental Science Nano

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As nanocomposite materials enter the marketplace, the entire life cycle of products, including end-of-life and reuse of scrap should be considered. The impact of recycling on CNT-filled polypropylene (PP) and human exposures was studied simultaneously by repeated injection molding. Addition of CNTs to PP increased the resistance to degradation of the PP. With the exception of grinding, where exposures to CNT-containing fragments and nanoparticles is a concern, addition of CNTs had no effect on nanoparticle exposures compared to neat polymer. This is a positive outcome for sustainability and reuse (compared to becoming scrap) of these materials for companies producing products with CNT-filled PP as there is little loss in properties with recycling and overall no impact on exposures.



## Environmental Science: Nano

## PAPER

## The Effects of Recycling on the Properties of Carbon Nanotube-Filled Polypropylene Composites and Worker Exposures

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Jinde Zhang,<sup>a</sup> Artee Panwar,<sup>a</sup> Dhimiter Bello,<sup>b</sup> Tim Jozokos<sup>d</sup> Jacqueline A. Isaacs,<sup>c</sup> Carol Barry,<sup>a</sup> Joey Mead,<sup>a</sup>

As nanocomposite materials enter the marketplace, it is critical to consider the entire life cycle of those products, including end of life and reuse of scrap. While recycling of polymer based materials is widely accepted for manufacturing and consumer scrap, the influence of the nanoscale filler on the recycling process has received little attention and may pose some unique challenges, such as the potential for human exposure to carbon nanotubes (CNTs) during the recycling process. In this work, the impact of recycling on CNT-filled polypropylene (PP) properties and exposures was studied by repeated injection molding and granulation up to twenty cycles, while simultaneously monitoring exposures. Characterization of chemical structure, melt rheology, mechanical properties, and morphology were performed on recycled materials. Both the neat and filled materials showed a reduction in viscosity with recycling, but the changes were greater for the neat materials. The mechanical properties (such as modulus, strength, toughness) were also affected by recycling. The Young's Modulus, yield strain and stress for both neat PP and CNT-filled PP were found to be little affected by recycling. Strain and stress at break for neat PP decreased with recycling, but only slight changes were found for the CNT-filled PP. The CNT-filled PP showed an increase in toughness with recycling due to changes in the crystallization behaviour. This offers potential for addition of CNTs for the purpose of improving recycling resistance. However, recycling should be performed under proper exposure controls because grinding generated high exposures to nanoparticles and CNT-containing respirable fibers.

### Introduction

In recent years, due to their multifunctional and intriguing properties, polymer composites are becoming more popular for components used in a wide range of applications, such as automotive, aerospace structural materials, and electronic devices.<sup>1-4</sup> Different polymer nanocomposites have been studied in the past few decades for a number of polymer matrices, including polystyrene (PS)<sup>5</sup>, polycarbonate (PC)<sup>6</sup>, poly(methyl methacrylate) (PMMA)<sup>7</sup>, polyamide<sup>8</sup>, polyethylene (PE)<sup>9</sup>, and polypropylene (PP)<sup>10</sup>. Among these polymer matrices, PP is widely used based on its superior mechanical properties, easy processability, and relatively low cost. These optimum properties give PP wide use in different fields, such as medical devices, food containers, and automotive interior

decorations. In addition to the polymer matrix, the type of nanometer-scale reinforcing particle in the nanocomposite plays a critical role. Nanoscale fillers have various shapes and sizes from spherical, plate-like, to fibers, and include nanoclays, silver nanoparticles, and carbon nanotubes (CNTs).<sup>11</sup> Compared to conventional microfillers used in polymer composites like talc, mica, and glass fibers, nanofillers can provide greater surface area and potentially superior mechanical properties or functionality at relatively low contents, a result of their nanoscale size and large aspect ratio.<sup>12-15</sup> CNTs are interesting because of their excellent mechanical properties (20 GPa tensile strength and almost 1 TPa modulus),<sup>16</sup> very large aspect ratio (100-1000),<sup>17</sup> as well as functional properties, such as electrical and thermal conductivity.<sup>18</sup> Therefore, considerable research has been performed on CNT reinforced polymer nanocomposites for various applications including electronics,<sup>19</sup> automotive,<sup>20</sup> and others.<sup>21</sup> Indeed, composites are a major end use for CNTs.

As CNT-filled PP begins to enter the marketplace, it is critical to consider the entire life cycle of the product, including end of life and reuse of scrap. While recycling of polymer based materials is widely accepted for both manufacturing and consumer scrap, nanocomposites pose some unique

<sup>a</sup> Center for High-rate Nanomanufacturing, University of Massachusetts Lowell.

<sup>b</sup> Department of Work Environment, University of Massachusetts Lowell.

<sup>c</sup> Northeastern University.

<sup>d</sup> Hyperion Catalysis International, Inc.

E-mail: [joey\\_mead@uml.edu](mailto:joey_mead@uml.edu)

Fax: +01 978-458-4141

challenges. The recycling behaviour of most polymers is well understood, but the influence of the nanoscale filler on the recycling process has received little attention and may differ from conventional filled polymers. As an example, the degree of dispersion could potentially increase yielding improved properties with additional recycling. More concerning is the potential for human exposure to CNTs and CNT-containing fragments during the recycling processes.<sup>22,23</sup>

Exposure data related to post-processing of CNT-enabled products remains limited. This is especially true for recycling and handling of nanowaste, and end-of-life disposal, for which there are practically no available data. Unique to this series of studies is simultaneous investigation for the first time of airborne nanoparticle and fiber exposures during injection molding and recycling (grinding) of carbon nanotube reinforced polypropylene composites (CNT-filled PP) relative to injection molding and recycling of baseline polypropylene (PP). Major findings from exposure assessment is summarized at the end of the 'results' section.

Mechanical recycling is regarded as the most popular approach to recycle conventional plastics (e.g. PP, PE, High impact polystyrene (HIPS), Acrylonitrile Butadiene Styrene (ABS), PS, and PC).<sup>24</sup> The effect of successive injection molding on the structure and properties of neat isotactic propylene was investigated by Aurrekoetxea et al.<sup>25</sup> Results indicated that the main impact of such reprocessing was a decrease in melt viscosity as a result of a reduction in molecular weight. They also found that recycling led to higher crystallization rates, crystallinity degree and crystallization temperature for PP, resulting in an increased elastic modulus and yield stress with recycling. Jin et al.<sup>26</sup> investigated the effect of successive extrusion (up to one hundred cycles) on the structure and properties of low density polyethylene (LDPE). They found that the melt viscosity of LDPE was increased by such successive extrusion due to the crosslinking reactions happening during processing. HIPS was studied by Brennan et al.<sup>27</sup> in order to evaluate the effect of recycling. Results showed that the main effect of recycling was a decrease in melt viscosity, strain at break, as well as impact strength due to the degradation in molecular weight. Perez et al.<sup>28</sup> studied the effect of reprocessing on the properties of ABS. Results showed that melt viscosity and tensile strength were not affected by the number of processing cycles, but the impact strength decreased slightly. Their results showed that ABS has good resistance to degradation by recycling, but that impact modifiers may be needed to improve impact strength after recycling. The degradation and recycling of an extrusion grade polycarbonate and the effect of the humidity have also been studied by La Mantia and Correnti.<sup>29</sup> The results showed that the effect of reprocessing on the properties of the recycled PC depended on the thermo-mechanical environment associated with the processing technique and included temperature, shear rate and pressure. The molecular weight of the polymer, the presence of moisture and the nature of the additives were also found to be important.

In general, thermoplastic recycling effects are very dependent on the specific polymer, the additives, as well as

processing conditions. With respect to viscosity and molecular weight, in most cases there is a reduction in both due to chain scission, but polymers such as LDPE undergo crosslinking reactions and thus have an increase in molecular weight and viscosity. Impact strength for both HIPS and ABS decreased with recycling. Additives can be used to improve properties of the recycle, but it is important to evaluate the behaviour for the specific material and process of interest. PP, the polymer of choice in this work shows a decrease in molecular weight with recycling.

Although some limited studies of nanocomposite recycling have been done, the bulk of the work in recycling of polymer-based nanomaterials has been primarily focused on nanoclay reinforcements. Jurado, et al.<sup>30</sup> studied polyamide nanocomposites and found improved mechanical properties with recycling as a result of greater exfoliation of the clay with recycling. This unusual effect for nanocomposites was also seen for poly (ethylene terephthalate) nanoclay composites<sup>31</sup> and polyamide nanoclay composites.<sup>32</sup> The effect of successive extrusion on the structure and properties of ABS/montmorillonite nanocomposites was investigated by Karahaliou et al.<sup>33</sup> It was found that reprocessing did not significantly change the rheological and tensile properties up to 5 cycles, even though oxidation of materials was found during recycling. Thompson et al.<sup>34</sup> studied the recyclability of a silica reinforced thermoplastic olefin elastomer and showed that although there was degradation occurring during recycling, the mechanical and rheological properties were still higher than those of the unfilled elastomer. Polyamide 6 nanocomposites were also studied by Goitisoló, et al.<sup>35</sup> in order to find the effect of successive injection molding up to five cycles on the structure and properties. This work demonstrated that no change in chemical structure or elastic properties occurred with recycling, but the viscosity of the composites decreased with recycling. Investigation on the effect of recycling on the structure and properties of PP/cloisite 15A nanocomposites was performed by Touatia et al.<sup>36</sup> They found that up to four cycles of internal mixing did not impact the chemical structure or storage modulus, but the melt viscosity decreased. While nanocomposite recycling shows some cases of improved properties with recycling, most of the previous work has investigated nanocomposites based on clay and limited up to 10 cycles.

To our knowledge, there are no reported studies on the recycling of CNT-filled polymers, particularly where dispersion of the original material is quite good and expected to play a minor role in the recycling behavior. In this paper, the effect of recycling on the structure and physical properties of CNT-filled PP was systematically studied by successive injection molding and granulating up to twenty cycles. Chemical structure, mechanical, and rheological properties were tested to quantify the effect of recycling. Concurrently, the exposure to CNTs was measured and is reported in a recently published paper.<sup>37</sup>

## Experimental

### Materials

CNT-filled PP with 20 wt. % of CNTs (MB3020-01) was provided by Hyperion Catalysis International.

The CNTs used in the PP composites were multiwall CNTs (MWCNTs). Characterization of the CNTs included transmission electron microscopy (TEM) for primary size and morphology, total and water-soluble metals by inductively coupled plasma mass spectrometry (ICP-MS) and organic and elemental carbon as described in detail elsewhere (Bello et al 2009<sup>38</sup>; Hsieh et al 2011<sup>39</sup>).

For morphological characterization, CNTs were dispersed at 1 mg per mL in 0.1 wt. % Triton-X 100 (a chemical surfactant) in deionized water for 10 min with 30 sec cycle cup sonication (~200 W) (Branson Sonifier S-450A, Branson Ultrasonics, Danbury, CT) (Pal et al 2014<sup>40</sup>). The dispersion was further diluted in deionized water to 50 µg per mL. The TEM samples were then prepared by drop casting CNT dispersions on TEM grids. The grids were allowed to air-dry before imaging by transmission electron microscopy (Phillips EM 400T). Twelve images were collected at different magnification levels. The original multiwall CNTs embedded in the composite were rope-like agglomerates, with an average outer tube diameter of 10 nm (range 4-20 nm), and ranging in length from <0.5 to ~5 µm (Figure 1 in supporting information).

Based on ICP-MS analysis, the most abundant elements in these CNTs were: iron (Fe, 0.65%); molybdenum (Mo, 0.14%) and aluminum (Al, 1.72%). Copper (Cu), zinc (Zn), manganese (Mn), tin (Sn) and chromium (Cr) were in the 3-5 µg/g (ppm). To dilute the masterbatch, neat polypropylene (Pro-fax PD702) supplied by Lyondellbasell was used. It had the same grade as neat PP used in the masterbatch preparation from Hyperion Catalysis.

#### Nanocomposite preparation

Nanocomposites with the desired CNT loading were made by the masterbatch dilution method. For this work, seven different loading levels from 1 to 20 wt. % CNT-filled PP were produced in an 18-mm diameter intermeshing co-rotating twin-screw extruder (Leistritz ZSE 18HP). The machine was operated at 200 rpm screw speed. The barrel temperature was set from 160 to 190°C in 5°C increments with a final temperature of 200°C from the feed zone to the die. The screw was specifically programmed at a moderate shearing profile in order to protect the CNTs from significant breakage during processing. After compounding, the viscosity of each composite was analyzed by Melt Flow Index (MFI) testing, according to ASTM D1238 under 230°C and 2.16-kg load. Based on the results of the MFI testing (Figure 1), it can be seen that the MFI drops from 33 g per 10 min to almost 0.84 g per 10 min with an increase in CNT loading from 0 wt. % to 5 wt. %. Above 5 wt. %, the melt viscosity of the composite was too high to process. The 3 wt. % was chosen because the MFI is typically 10 or higher for injection molding<sup>41</sup> and it had the highest loading of CNTs.

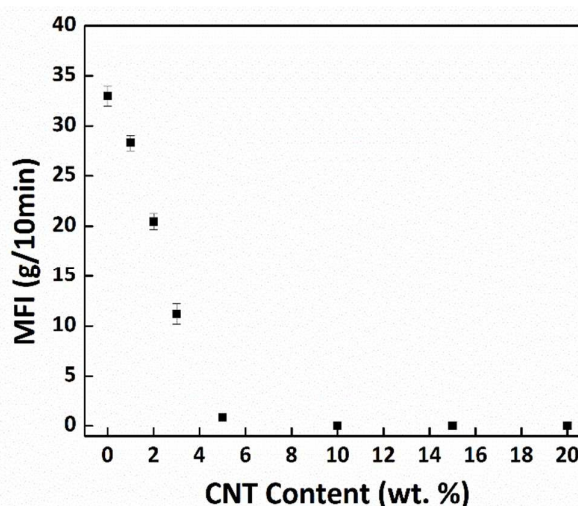


Figure 1. The MFI values for CNT-filled PP at different CNT loadings.

#### Recycling

Recycling of 3 wt. % CNT-filled PP was carried out via injection molding and granulating. 20 Kg of 3 wt. % CNT-filled PP from the same batch of extrusion compounding was injection molded (Arburg 320C) into tensile and flexural bars as per ASTM standard sizes. The mold temperature was 25°C. The barrel temperature was set from 230 to 190°C in 10°C increments from the nozzle to the feed zone. The screw speed was 200 rpm. After molding, a certain number of tensile and flexural bars were reserved and conditioned at 25°C and 40 % relative humidity for 48 hrs. The rest of the samples were ground into small particles using a granulator (Cincinnati Milacron TF 58) with a 10-mm screen. This was considered one full cycle. Recycling was repeated up to 20 cycles to fully investigate the effect of recycling on the structure and properties of the composites. Both the neat PP and CNT-filled PP (3 wt. %) were recycled under these conditions.

#### Chemical structural characterization

Infrared spectroscopy was measured by attenuated total reflection (ATR) method on tensile bars molded by injection molding after conditioning at 25°C and 40 % relative humidity for 48 hrs. The machine was a Nicolet 4700 FT-IR. The scanning wavelength ranged from 4000 to 400 cm<sup>-1</sup>.

#### Rheological characterization

The effect of recycling on the melt viscosity, was analyzed by Melt Flow Index (MFI) measurement using a Dynisco D4001. The testing conditions were 230°C temperature and 2.16-kg load according to ASTM D1238. A capillary rheometer (Dynisco LCR 7000) was also used to study the rheological behaviour of materials as a function of shear rate. Reground material after every other recycling cycle was used for rheological properties.

#### Mechanical Properties Testing

Tensile properties were measured on the samples from injection molding using an Instron 6205 universal testing

machine. The samples were molded into dumbbell shapes with length 165 mm, width 12.9 mm and thickness 3.2 mm according to ASTM D638. Samples were stretched at a crosshead rate of 100 mm per minute with an extensometer attached on them. Notched Izod impact testing was also carried out on rectangular shaped specimens [3.23×12.86×65 mm] using an impact tester (TMI NO. 43-1) based on ASTM D256. A notch of 2 mm depth with a 45° angle was cut using a notch cutter. Ten specimens for each sample were tested.

#### Morphological characterization

Transmission electron microscopy (TEM) was used to obtain images on microtomed samples (~200 nm thick) using a Philips EM400T at an accelerating voltage of 100 kV to study the dispersion of CNTs in PP.

#### Differential scanning calorimetry

Differential scanning calorimetry (DSC) (TA Q300) was used to study the crystallization behaviour of PP and CNT-filled PP. About 7-12 mg of samples from the regrind were encapsulated in an aluminium closed pan before testing and then heated to 200°C in a nitrogen atmosphere at a rate of 10°C per min to erase any thermal history and residual stress in the sample, and then cooled down to -50°C at a rate of 10°C per min to record the crystallization behaviour.

#### Exposure characterization

Exposure characterization focused on source emissions during loading, melting, molding, grinding and recycling of scrap material over twenty cycles and included real time characterization of total particle number concentration and size distribution, nanoparticle and fiber morphology, as well as operator's personal fiber exposures utilizing a suite of real-time instruments, integrated sampling, and extensive electron microscopy to classify and quantify respirable fibers. Detailed exposure information associated with this work can be found in Boonruksa et al.<sup>22</sup>

## Results and discussion

#### Chemical structural characterization

Infrared (IR) spectroscopy is a simple and reliable technique widely used to analyze any chemical structural changes in materials. The high temperatures and intensive shearing stresses during recycling can promote the degradation of the polymer chain, which can happen via various mechanisms, such as thermal, mechanical, oxidative, or combinations of these degradation mechanisms.<sup>25</sup> The presence of tertiary carbons in PP can induce rapid oxidation.<sup>42</sup> Widespread degradation will result in changes in the chemical structure, which would be found in the IR spectra. However, from the results of ATR-IR testing shown in Figure 2, there were no significant variations found in the spectra for either neat PP or CNT-filled PP with recycling. This lack of change in the spectra shows that there were insignificant oxidative reactions during recycling. This is probably due to the absence of oxygen in the polymer melt. A similar result was also found by Aurrekoetxea, et al.<sup>25</sup>

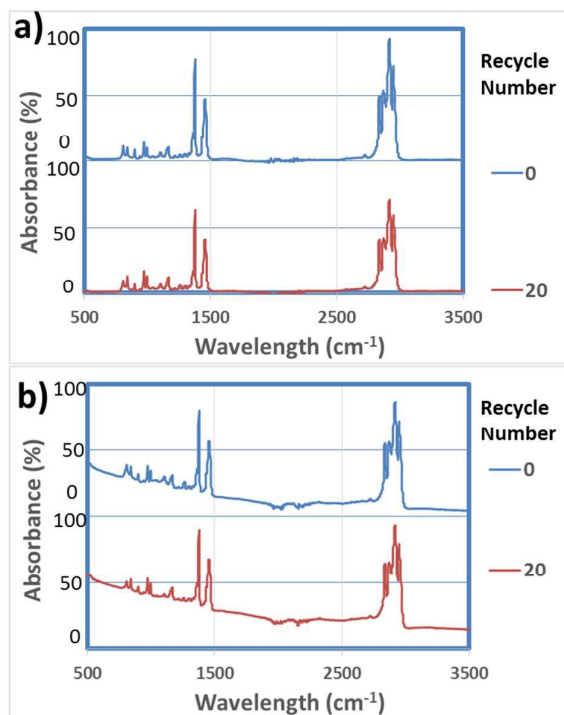


Figure 2. ATR results for recycled (a) neat PP and (b) 3 wt. % CNT-filled PP.

#### Rheological characterization

Although there was no significant change in chemical structure for either neat PP or CNT-filled PP under the high processing temperature and shear stresses of repeated injection molding and grinding during recycling, the polymer chains may break resulting in decreased molecular weight. This can be measured by the MFI. Melt flow rate is an indirect measure of molecular weight, with high melt flow rate corresponding to low molecular weight.<sup>25</sup> The MFI values for both neat PP and CNT-filled PP materials (Figure 3) increased with recycling. This means the molecular weight for both neat PP and CNT-filled PP was reduced during recycling. Combined with the results of IR testing, we can conclude that chain scission occurs, but there does not appear to be significant oxidation. The extent of the degradation will depend on the specific processing conditions, such as barrel temperature, screw speed, injection velocity, and material type. It also can be seen in Figure 4 that the susceptibility to degradation was different for neat PP and the CNT-filled PP material. The MFI of neat PP showed a much steeper change as compared to the CNT-filled PP. The CNT-filled PP showed greater resistance to degradation from recycling as compared to the neat PP as evidenced by the lower change in MFI with recycle number for the CNT-filled PP as compared to the neat PP. This difference in degradation resistance can lead to different mechanical property behavior.

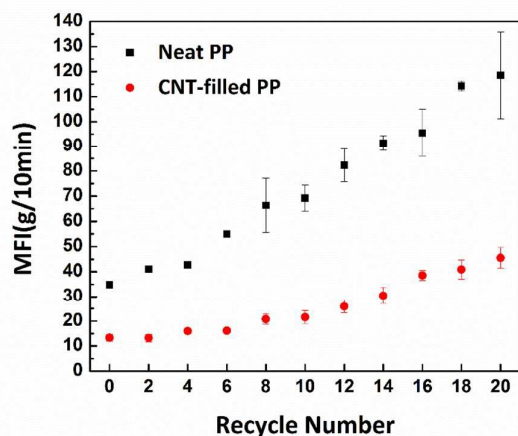


Figure 3. MFI for recycled neat PP and 3 wt. % CNT-filled PP.

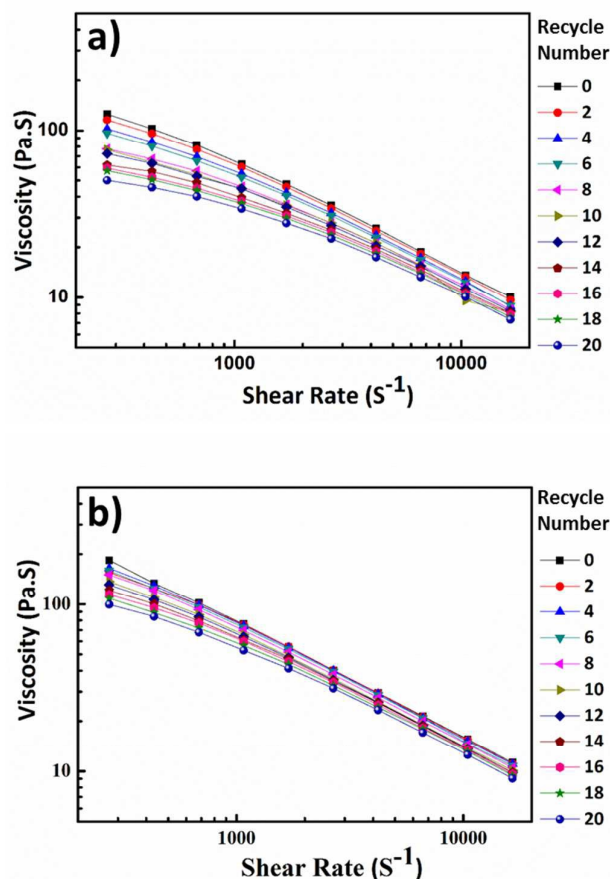


Figure 4. Capillary rheology results for recycled (a) neat PP and (b) 3 wt. % CNT-filled PP.

In addition to MFI testing, capillary rheological testing was performed and is presented in Figure 4. Shear thinning behaviour was present for both neat PP and CNT-filled PP. The power law index for both materials increased slightly with

recycling. Recycling decreased the viscosity for both neat PP and CNT-filled PP, but the viscosity in the low shear rate region ( $<1000 \text{ S}^{-1}$ ) exhibited more sensitivity to recycling. This is because the low shear rate viscosity is more dependent on the molecular weight of polymer. It was also found (Figure 4) that the change in viscosity with recycling over the full range of shear rates was less for CNT-filled PP as compared to that of neat PP, consistent with the behaviour seen in the MFI testing.

#### Mechanical properties characterization

CNTs can significantly improve the mechanical properties of a polymer due to the CNT's extremely high Young's Modulus and tensile strength.<sup>16</sup> The addition of 3 wt. % CNTs to the PP matrix increased the Young's Modulus from 1570 MPa for neat PP up to almost 4000 MPa for the filled materials (supporting information Figure 2, zero recycle number). In addition to enhancing the Young's Modulus, the CNT reinforcement also increases the stress at yield. The tensile stress at yield of neat PP was enhanced from 34 MPa to about 40 MPa with the addition 3 wt. % CNTs (supporting information Figure 3). Similar results for the CNT reinforcement effect on PP have been reported in the literature.<sup>43-47</sup>

Although the rheological measurements showed degradation for both neat PP and CNT-filled PP, neither the Young's Modulus or the tensile stress and strain at yield exhibited significant changes as a function of recycling (supporting information Figure 2, 3, and 4). This is because these three properties are considered small strain properties, which have only very slight dependence on the molecular weight.<sup>48</sup> Therefore, degradation by molecular weight reduction from recycling would be expected to have only a slight impact on these properties.

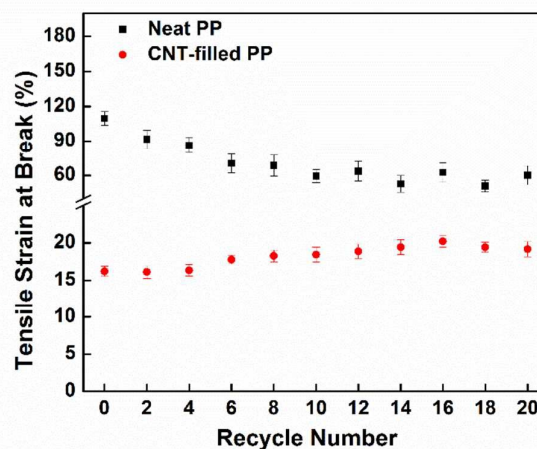


Figure 5. The tensile strain at break for recycled neat PP and 3 wt. % CNT-filled PP.

For properties related to larger deformation, such as tensile strain at break (Figure 5), the effect of recycling was more apparent. The lower molecular weight from degradation during recycling causes reduced entanglement of the polymer

chains leading to lower strain at break.<sup>25</sup> There is a decrease in tensile strain at break for neat PP after 20 cycles of processing (Figure 5). However, for 3 wt. % CNT-filled PP, recycling gave a slight increase in the tensile strain at break. (Neither composition showed a significant change in tensile stress at break shown in supporting information Figure 5). As noted in the rheology data, the addition of CNTs to the polymer matrix increases the resistance of PP to degradation in molecular weight by recycling. Thus, the greater resistance to molecular weight breakdown, as well as the changes in crystallization behaviour (discussed below), provide good tensile strain at break in the 3 wt. % CNT-filled PP as compared to the neat PP.

Izod impact testing was performed for both neat PP and CNT-filled PP to evaluate the effect of recycling on the impact resistance. The Izod impact resistance reflects the ability of a material to absorb impact energy, which can be influenced by the molecular weight.<sup>25</sup> Since recycling can break the molecular chains and lead to decreased molecular weight of the polymer, this can reduce the impact resistance of the material.<sup>25</sup> The impact resistance for neat PP decreased with recycling (Figure 6), but the impact resistance of the CNT-filled PP material remained essentially constant. Consistent with the tensile data, the addition of CNTs to the PP matrix led to better resistance to degradation by recycling as compared to the neat PP.

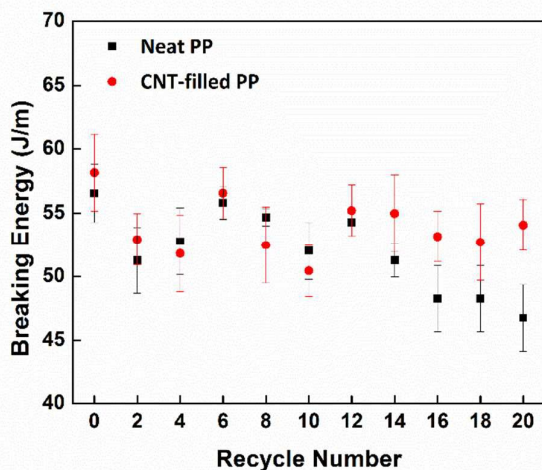


Figure 6. Izod impact resistance of recycled neat PP and 3 wt. % CNT-filled PP.

From these results, it can be concluded that the addition of CNTs to PP increases the resistance to degradation by recycling of the PP matrix. This suggests that the addition of CNTs to the polymer matrix not only increases mechanical properties, but also results in improved recycling resistance. A further explanation for this behaviour is given below.

#### Crystalline behaviour characterization

While there are no reports on the impact of recycling on CNT-filled PP, there are considerable reports on the toughening effect of CNT on polymers.<sup>49-51</sup> From those reports, nanotube breakage and pull-out, along with secondary crystallites increase the toughness of CNT-filled polymers. In this paper, to determine why recycling had less effect on the 3 wt. % CNT-filled PP as compared to neat PP, DSC was carried out on recycled CNT-filled PP and neat PP samples. The crystallization temperature ( $T_c$ ) can be determined directly in the DSC curve. The degree of crystallinity ( $X_c$ ) can also be obtained from the area under the curve by calculation using equation 1<sup>52</sup>;

$$X_c = \frac{\Delta H_f}{\Delta H_f^0(1-\phi)} \times 100 \quad (1)$$

where  $1-\phi$  is the weight fraction of polymer and  $\Delta H_f^0$  is the theoretical enthalpy value for 100% crystalline PP, which is taken to be 209 J per g.<sup>53</sup> A summary of DSC results is presented in Figures 7 and 8 (also listed in Tables 1 and 2). The crystallinity degree and crystallization temperature for neat PP (Figure 7 and Table 1) showed little effect from recycling, which was also reported by other researchers.<sup>48</sup> However, for 3 wt. % CNT-filled PP,  $T_c$  shifted to 9°C higher in temperature (Figure 8 and Table 2). This can be attributed to the heterogeneous nucleation effect of the CNTs, which facilitate the crystallization of PP chains when the nanocomposite is cooled down from a temperature above its melting point.<sup>54</sup> Percent crystallinity also increases from 49% for neat PP to 52% for 3 wt. % CNT-filled PP (zero recycling runs for both), confirming the heterogeneous nucleation effect.

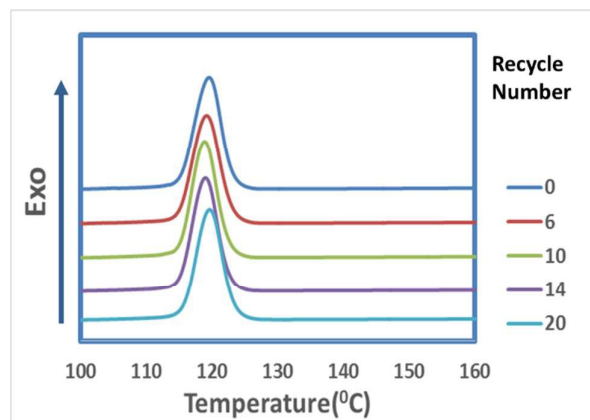


Figure 7. DSC results for recycled neat PP.



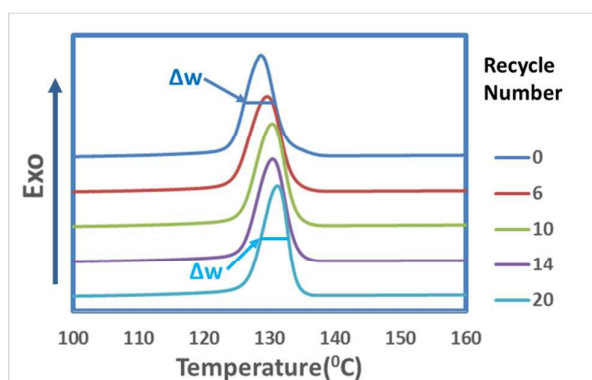


Figure 8. DSC results for recycled CNT-filled PP.

**Table 1** Crystallization parameters for recycled neat PP

Recycle Number	$X_c$ (%)	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta w$ ( $^{\circ}\text{C}$ )
0	48.8	119.5	5.7
6	48.2	119.2	5.8
10	47.9	118.9	5.7
14	47.6	119.0	5.7
20	47.6	119.6	5.8

**Table 2** Crystallization parameters for recycled 3 wt. % CNT-filled PP

Recycle Number	$X_c$ (%)	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta w$ ( $^{\circ}\text{C}$ )
0	51.5	128.7	6.8
6	51.5	129.6	6.3
10	51.0	130.4	6.2
14	50.3	130.5	6.0
20	49.2	131.2	5.5

This heterogeneous nucleation is affected by recycling. The  $T_c$  of CNT-filled PP increased with recycling (Figure 8), showing that recycling enhanced the heterogeneous nucleation effect. In addition to increasing  $T_c$ , such enhanced nucleation effects also lead to narrower spherulite size distribution. The width at half-height of the exothermic peak,  $\Delta w$ , can be used to characterize the spherulite size distribution.<sup>54</sup> Smaller width values indicate narrower size distributions, while wider values indicate a wider size distribution.<sup>54</sup> With recycling,  $\Delta w$  was reduced (shown in Table 2), indicating that the spherulite size distribution became narrower with recycling (Figure 8). The increasing  $T_c$  and decreasing  $\Delta w$  both show that recycling enhanced the CNT nucleation effect for CNT-filled PP. This could be because recycling breaks the CNT length, producing more, but shorter tubes under the high shearing stress. The recycling could also improve CNT dispersion.<sup>55</sup> The change in mechanical properties is explained by the more uniform spherulite size distribution, which leads to improved mechanical properties by reducing the level of stress concentrations for the CNT-filled PP.<sup>52</sup>

### Morphological characterization

As one potential explanation for the improved mechanical properties is improved dispersion, TEM analysis was performed on the masterbatch and as a function of recycling. The TEM images for the master batch of 20 wt. % CNT-filled PP directly from the supplier (Figure 6, supporting information) demonstrated that the dispersion of the CNTs in the PP was very good. After let-down through the twin screw extrusion process, the 3 wt. % CNT-filled PP still showed good dispersion with some agglomerates by TEM analysis (Figure 7, supporting information). With recycling there was no clear change in dispersion by TEM analysis despite the changes in crystallization behaviour (Figure 7, supporting information). Other methods of analysis may be required to fully elucidate possible changes in dispersion.

### Impact of recycling on exposures

The main findings of exposure characterization, details of which have been published elsewhere, can be summarized as follows:

- 1) Hot processes, such as melting and molding, generated exclusively nanoparticles originating from the condensation of semi-volatile organics (SVOCs), regardless of the composite type (CNT-filled PP or PP). Total airborne nanoparticle concentration during loading, melting, and molding of CNT-filled PP composites with the equipment ventilation on, had geometric mean (GM) ranging from  $1.2 \times 10^3$  to  $1.6 \times 10^4$  particles per  $\text{cm}^3$  for CNT-PP, and from  $1.9 \times 10^3$  to  $7.1 \times 10^3$  particles per  $\text{cm}^3$  for PP composites. The process to background (P/B) GM ratios varied from 1.0 to 2.9. These exposure levels were not statistically significantly different from the respective injection molding steps of pure PP composites. Furthermore, the number of recycling runs did not have any impact on emissions and exposures. Therefore, addition of CNTs into PP did not have any notable impact on the emission of nanoparticles.
- 2) Grinding of CNT-filled PP composites generated much higher exposures to nanoscale and microscale particles than synthesis steps. The total particle number GM ranged from 60,000 to 433,000 particles per  $\text{cm}^3$ , with maxima of 1.1 million particles per  $\text{cm}^3$ . The process to background GM ratio varied from 9.5-301. Grinding of reference PP composites generated similarly high exposures, with GM ranging from 6300 to 676,000 particles per  $\text{cm}^3$ , and peak maxima over 1.9 million particles per  $\text{cm}^3$ . These values were generally in the same range as CNT-filled PP composites, albeit slightly higher. Again, there was no trend in exposures relative to recycling run and no statistical differences between the processing of CNT-filled PP composites and PP. Larger microscale particles were observed only during grinding and loading of the reground material, but numbers were generally low (<30 particles per  $\text{cm}^3$ ).
- 3) No free CNTs were found in the transmission electron microscopy (TEM) grids collected during all processes.

4) Respirable fibers were generated during grinding of CNT-filled PP, as well as neat PP, but not during injection molding. The concentration of long respirable fibers, (defined as  $>5\mu\text{m}$  in length and aspect ratio  $>3$ ) was generally low (0-0.2 fibers per  $\text{cm}^3$ ) during grinding of CNT-filled PP and 0-0.35 fibers per  $\text{cm}^3$  for neat PP. The concentration of short respirable fibers ( $<5\mu\text{m}$  in length and aspect ratio  $>3$ ) generated during grinding was 0.26-0.7 and 0.03-0.37 fibers per  $\text{cm}^3$  for CNT-filled PP and neat PP, respectively. There was some suggestive evidence that the concentration of short fibers increased with the number of recycling runs (Boonruksa et al.<sup>22</sup>).

4) The number of recycling runs applied to the CNT-filled PP nanocomposite (up to 20) had no significant impact on overall exposures (nanoparticles, microscale particles and long respirable fibers) during injection molding, loading, and grinding.

5) The airborne respirable dust (and fibers) generated during grinding was also analyzed for CNTs using the NIOSH thermogravimetric analysis method 5040. The CNT content in the airborne respirable dust was 2.9 wt. %, very close to the expected 3 wt. % CNT. We should be mindful that even at 0.2 fibers per  $\text{cm}^3$ , millions of CNTs may be present in the respirable dust generated during grinding. Because larger scale industrial processes may generate much higher fiber levels than those measured in this study, engineering controls of exposures are strongly recommended during grinding/recycling as well as during handling of recycled CNT-PP composite dust.

6) The exact chemical composition of airborne nanoparticles generated during injection molding of CNT-filled PP and neat PP remains poorly understood. Given that these nanoparticles

represent the major exposures during injection molding (and extrusion) of such nanocomposites, further research into the chemical composition of the emitted nanoparticles is warranted. A study on the chemistry of VOCs emissions during processing of common polymer materials by Unwin et al.<sup>56</sup> suggests potential for emission of a range of compounds harmful by inhalation (R20) and/or irritating to the respiratory system, eyes and skin (R36/38). Authors found generally low levels of formaldehyde ( $<7\mu\text{g per m}^3$ ), naphthalene ( $<1\text{ ng per m}^3$ ), and other polycyclic aromatic hydrocarbons (PAHs,  $<1\text{ ng per m}^3$ ). In a chamber study, they found emission of alkenes and small size alkanes, such as butane and pentane. The performance characterization in this study suggests polymeric chain breaking, consistent with findings of Unwin et al. However, much higher chain alkenes and associated oxidation by-products are likely being generated. There is a clear need for further detailed characterization of the chemical composition of the PP polymer fumes.

7) Toxicology of these polymeric fumes and other CNT-containing fragments has not been studied. To date, the information on the biopersistence and toxicity of particles or fibers with embedded CNTs is limited (Nowack et al.)<sup>57</sup> and suggest that, at least initially, the toxicology of released composite particles is governed primarily by the properties of the composite matrix. Therefore, studies focusing on toxicological assessment of fibers and nanoparticles generated during realistic exposure scenarios along the life-cycle of nanocomposites containing CNTs are required and are being currently researched in our lab.

## Conclusion

For both neat PP and CNT-filled PP, the chemical structure did not exhibit significant changes after recycling. The main effect of recycling on PP and CNT-filled PP was a decrease in melt viscosity due to degradation from chain breakage. Viscosity was found to decrease for both neat and filled materials, but the changes were greater for the neat material. The mechanical properties (such as modulus, strength, toughness) were also affected by recycling. Those properties related to small strain or elongation, such as Young's Modulus, yield strain and stress for both neat PP and CNT-filled PP were found to be little affected by recycling. The properties related to large strain, such as strain and stress at break for neat PP were decreased by recycling. In contrast, recycling brought only very slight changes to the mechanical properties for the CNT-filled PP materials. The CNT-filled PP materials showed an increase in toughness with recycling. DSC analysis showed this was due to changes in the crystallization behaviour of CNT-filled PP materials with recycling. Recycling improved the secondary nucleation effect induced by CNTs in the PP, which can refine the spherules' size distribution and therefore toughened CNT-filled PP. We conclude the addition of CNT to PP increases the resistance to degradation of the PP. This offers potential for addition of CNTs for the purpose of improving recycling

resistance. Moreover, this is positive for sustainability and reuse of these materials for companies producing products with CNT-filled PP as there is little loss in properties with recycling. Scrap from the manufacturing process may be incorporated/reused without significant loss in tensile properties, thus facilitating reuse back into the original product as opposed to lower end applications or becoming scrap material.

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