# The Effects of Recycling on the Structure and Properties of Carbon Nanotube-Filled Polycarbonate

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## Abstract

Sustainable manufacturing processes are becoming more important in industrial practice. A critical part of the manufacturing process is understanding the recycling behavior of nanocomposite materials, particularly as more recycled plastic nanocomposites are entering the market for a variety of different applications. A common method to recycle thermoplastic composites is by melting and remolding, which often leads to decreased mechanical properties. This work was conducted to investigate the effect of nanofillers on the recycling behavior and structure-property relationships of carbon nanotube (CNT)-filled polycarbonate (PC). Materials were recycled by repeated injection molding and granulating up to twenty cycles. The effect of recycling on chemical, rheological and mechanical properties was investigated. The results indicated a general decrease in melt viscosity and mechanical properties (with the exception of Young's Modulus). The CNT-filled PC shows less resistance to recycling compared to neat PC

## 1. Introduction

Polymer composites composed of a polymer matrix and organic or inorganic fillers are commonly used in diverse applications including sporting goods, aerospace components, and automotive. The popularity of polymeric nanocomposites can be ascribed to their superior properties compared to conventional polymer and polymer composite materials. These improved properties are often obtained at much lower loading levels compared to conventional filled materials, a result of the increased surface area of the nanoscale filler. These properties include superior barrier capability, excellent mechanical stiffness and strength, adjustable thermal or electrical conductivity, and anti-bacterial behavior.[1,2,3,4] The choice of the specific nanoscale fillers based on the application and polymer matrix choice. Among the nanoscale fillers, carbon nanotubes (CNTs) are of increasing interest, since 1991 when CNTs were first documented by Iijima[5]. Compared to conventional microfillers like talc, mica, glass fiber, carbon blacks, etc., which require the addition of nearly 20-30 wt. % into the polymer matrix in order to achieve superior mechanical properties [6], CNTs can improve a polymer's mechanical properties at remarkably low loadings (< 3 wt. %). This is because of the high aspect ratio (100-1000) and high surface area of the CNTs. As CNT-filled PC begins to enter the marketplace, the entire life cycle of the product including end of life and reuse of scrap must be studied. While recycling of polymer based materials is widely accepted for both manufacturing and consumer scrap, nanocomposites pose some unique challenges. The recycling behavior 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. For example, the degree of dispersion could potentially increase with the additional processing steps in recycling, which could yield improved properties. Our previous study about the effect of recycling on CNT-filled PP showed that CNT-filled PP had higher resistance to recycling compared to neat PP due to improved crystallization behaviour as recycling [7]. Studies of recycling of polycarbonate began nearly twenty years ago and are still of interest. Long and Soko[8] studied the hydrolytic degradation that occurs during molding polycarbonate. They reported that molding with excess moisture content caused chemical and physical degradation resulting in reduction in the tensile impact strength and tensile elongation. The effect of recycling on the properties of injection molded polycarbonate and glass fiber reinforced polycarbonate was also investigated by Abbas et al. [9]. It was reported that the glass reinforced grades exhibited degradation rates that were at least twice as high as that of an unreinforced polymer. This difference was most probably the result of greater viscous heating in the glass-reinforced systems. La Mantia and Correnti [10] focused their study on the effect of humidity on the degradation of PC during extrusion. Their work showed that the chain scission was strongly reduced if the processing was carried out under nitrogen flow. In these conditions less degradation effects were also observed for the dry material. Bernardo et al.[11] evaluated effect of recycling on the mechanical properties of fiber reinforced PC and found that the effects of recycling on the structure and properties of PC and its composites were highly dependent on the thermo-mechanical recycling environment for the process, including the temperature, shear rate, and pressure. The molecular weight of the polymer, the presence of moisture, and the nature of the additives were also important. For a typical process that uses recyclate material, the typical loading of recyclate does not exceed 25%.[12] An understanding of the effect of recycling runs on the material properties will determine exactly how much recyclate can be used back in the process. To our knowledge, there are no reported studies on the recycling of CNT-filled PC, 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 PC 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.

## 2. Experimental

### 2.1. Materials and CNT-filled PC preparation

 TechConnect Briefs 2017, TechConnect.org, ISBN 978-0-9975117-9-6

In this work, a masterbatch of 15 wt. % MWCNTs-filled PC (MB6015-00) was provided by Hyperion Catalysis International, Cambridge, MA. Based on the data sheet provided by company, the CNTs were multi-walled with a diameter around 5 nm [13]. To make materials, a twin screw extruder (Leistritz ZSE 18HP) was used to dilute the CNTs' concentration by compounding the masterbatch with neat PC (Mitsubishi Iupilon H-3000R) (same resin as used in the masterbatch). The screw was specifically programmed at a moderate shearing profile in order to protect the CNTs from significant breakage during processing. The screw speed was set to 300 rpm and barrel temperatures were set to 210, 225, 240, 245, 250, 260, 270, 275 °C from feed zone to the die. After compounding, the melt viscosity of each composite was measured via Melt Flow Index (MFI) testing according to ASTM standard D1238 under 300°C and 1.1-kg load. According to the results of MFI testing (see Figure 1), the MFI decreased from 45 g per 10 min to 8 g per 10 min when the CNTs' concentration increased up to 3 wt. % from 0 wt. %. Above 3 wt. %, the melt viscosity of CNT-filled PC became too high to be processed. The 3 wt. % was chosen for further studies because this was the highest loading of CNTs that could be processed by injection molding[14].

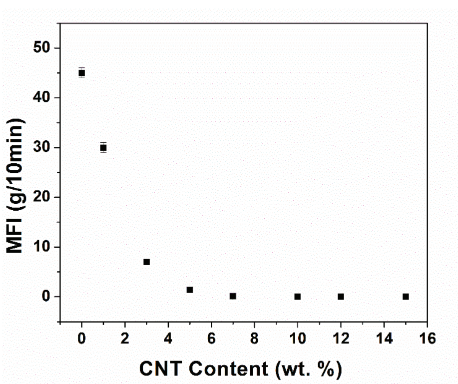


Figure 1. The MFI values for CNT-filled PC at different CNT loadings.

### 2.2. Recycling-injection molding and granulating

Recycling of CNT-filled PC (3 wt. %) was carried out via injection molding and granulating. 20-Kg CNT-filled PC (3 wt. %) prepared by twin screw compounding was injection molded (Arburg 320C) into tensile and flexural bars according to ASTM standard sizes. The barrel temperature for the injection molding machine (Arburg 320C) was set to 300, 290, 270, 260, 250 °C from nozzle to feed zone, while the hopper zone temperature was 23°C. The screw speed was 200 rpm. Injection velocity was 17cm$^3$ per second and the back pressure was set to 80 Bars. Decompression was 3 cm$^3$. After molding, a certain number of tensile and flexural bars were reserved and conditioned under 25 °C and 40 % relative humidity for 48 hrs. The rest of the samples were grounded into small particles via a granulator (Cincinnati Milacron TF 58) with 10-mm screen. This was considered one full cycle. This recycling process was repeated up to 20 cycles to evaluate the impact of recycling on the structure and properties of CNT-filled PC. Both neat PC and the CNT-filled PC (3 wt. %) were evaluated by this same procedure.

### 2.3. Characterization

Attenuated total reflection (ATR) was used for the infrared spectroscopy characterization of the chemical structure of recycled materials. Samples for testing were from tensile bars. The machine model was a Nicolet 4700 FT-IR and the scanning wavelength ranged from 4000 cm$^{-1}$ to 400 cm$^{-1}$. The effect of recycling on melt viscosity was analyzed by Melt Flow Index (MFI) measurements using a Dynisco D4001. The testing conditions were 300 °C temperature and 1.1-kg load (as per ASTM D1238). The reground material after every other recycling run was used to study the rheological properties. Tensile properties were measured on tensile bars using an Instron 6205 universal testing machine. Samples were molded into dumbbell shapes with a length of 165 mm, width of 12.89 mm, and a thickness of 3.23 mm according to ASTM D638. Samples were pulled at a crosshead rate of 100 mm per minute with an extensometer attached to measure strain.

## 3. Results and Discussion

### 3.1. Chemical Structure Characterization

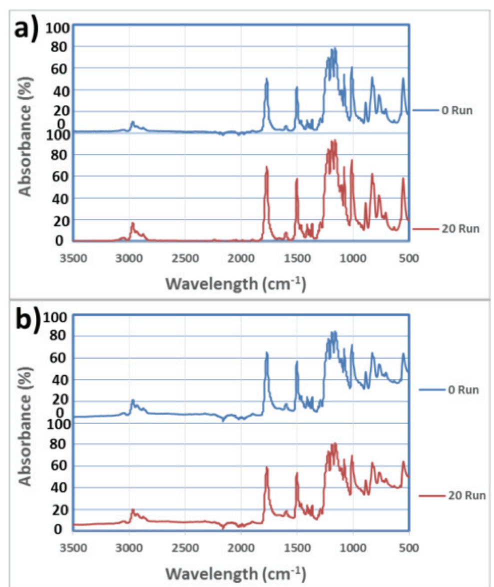


Figure 2. ATR-IR results for recycled (a) neat PC and (b) 3 wt. % CNT-filled PC.

Infrared (IR) spectroscopy is a typical method to identify different molecular structures or changes in molecular structure. The location and intensity of the peaks can be used to characterize the structure of a material. Intensive shear stress under relatively high temperature during recycling can promote the degradation of polymer chains.[15] Significant degradation will result in chemical structure changes, which would be detected in IR spectra. From the results of ATR-IR testing (Figure 2), there were no significant variations in IR spectra found for either neat PC or 3 wt. % CNT-filled PC. This lack of change shows that there was no significant change in chemical structure of both neat PC and CNT-filled PC with recycling.

### 3.2. Rheological Characterization

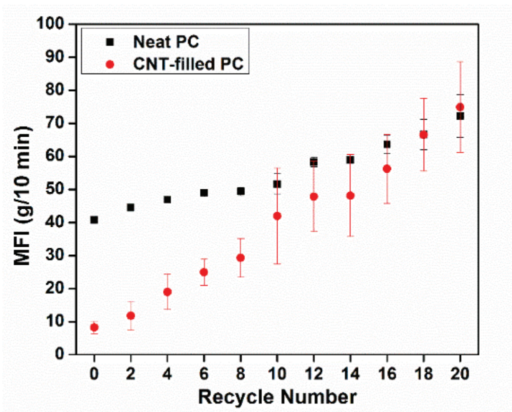


Figure 3. MFI for recycled neat PC and 3 wt. % CNT-filled PC.

Although there were no significant changes in chemical structure for either neat PC or 3 wt. % CNT-filled PC with recycling, degradation may happen by chain breakage resulting in lower molecular weight. This can be detected by MFI measurements. Melt flow rate is an indirect measure of molecular weight, with high melt flow rate corresponding to low molecular weight. From results shown in Figure 3, it can be seen that MFI for both neat PC and 3 wt. % CNT-filled PC increased with recycling. Thus, it is apparent that chain scission occurs leading to a reduction in molecular weight and lower viscosity. Figure 3 shows that the susceptibility to degradation was different for neat PC and the CNT-filled PC material. The MFI for CNT-filled PC shows a much steeper change with recycling compared to neat PC. This large change in melt viscosity means that CNT-filled PC shows less resistance to recycling compared to neat PC. The MFI for neat PC before recycling was about 40 g per 10 min, while for 3 wt. % CNT-filled PC prior to recycling, it was no more than 10 g per 10 min. Thus, the melt viscosity of 3 wt. % CNT-filled PC was much higher compared to neat PC as would be expected for a CNT filled material

### 3.3. Mechanical Properties Characterization

Young's Modulus is used to characterize the low strain behavior of materials. Because of CNT's extremely high modulus, the 3 wt. % CNT-filled PC has a significantly high modulus (almost 6000 MPa) compared to neat PC (about 2600 MPa) (Figure 4). With recycling, the Young's Modulus of CNT-filled PC decreased slightly, possibly due to breaking of CNTs during recycling. Although degradation was occurring with recycling, the 3 wt. % CNT-filled PC after 20 runs' recycling still possessed 5000-MPa Young's Modulus (See Figure 4), which is high enough for most applications. Compared to CNT-filled PC, neat PC showed less change with recycling, particularly after 10 runs' recycling.

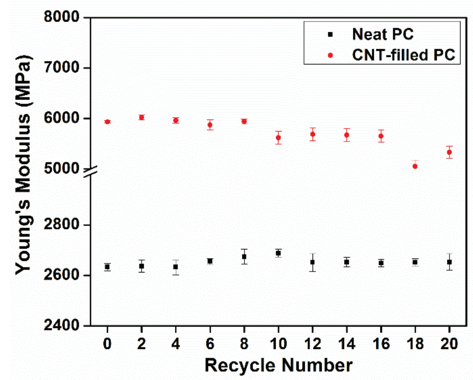


Figure 4. Young's Modulus of recycled neat PC and 3 wt. % CNT-filled PC.

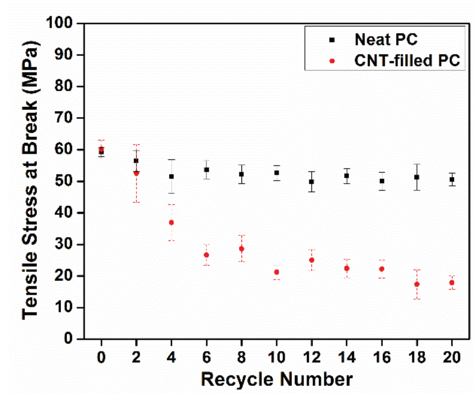


Figure 5. The tensile stress at break of recycled neat PC and 3 wt. % CNT-filled PC.

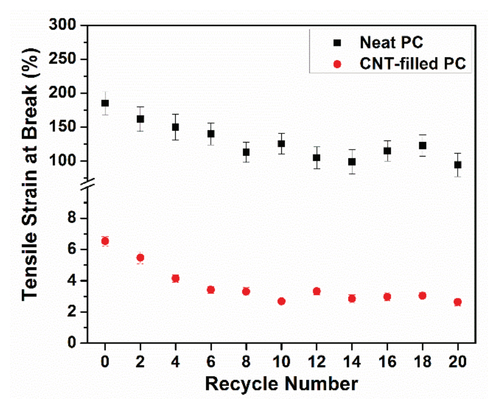


Figure 6. The tensile strain at break of recycled neat PC and 3 wt. % CNT-filled PC.

Compared to Young's Modulus, a more pronounced influence of recycling was observed on the failure properties, such as tensile stress and strain at break and strain energy at break (toughness). From Figure 6 it can be concluded that with the addition of 3 wt. % CNT did not improve the strength of PC. Similar results were also reported in other CNT-filled PC composites made by masterbatch dilution using similar materials[16]. In that work it was reported that there was a tough-to-brittle transition in the CNT-filled PC composites with increasing CNT content, occurring about 2 wt. %. Beyond this transition, the CNT-filled PC composites became more brittle due to poor CNT dispersion and local stress concentrations. In our work, the CNT concentration is 3 wt. %, which is beyond this transition point. Thus the addition of 3 wt. % CNTs did not increase the tensile stress at break for PC, but did enhance Young's Modulus. Compared to neat PC, the tensile strength for 3 wt. % CNT-filled PC decreased much more with recycling (see Figure 5). After 20 runs' recycling, the remaining tensile strength for 3 wt. % CNT-filled PC was only 18 MPa, which is much lower compared to the 51 MPa remaining tensile strength for neat PC with the same number of recycling runs. The tensile strain at break (Figure 6) showed similar results. The strain at break was reduced for the 3 wt% CNT-filled PC as compared to the pure PC, as expected for a CNT filled polymer. The strain at break was reduced with number of recycling runs for both neat PC and 3 wt% CNT-filled PC. In general, 3 wt. % CNT-filled PC experienced more degradation in tensile properties with recycling as compared to neat PC. These results are consistent with the rheology analysis. The increased degradation in molecularweight for the 3 wt. % CNT-filled PC may be due to the overall higher melt viscosity compared to neat PC, providing greater shear stresses in the compound and contributing to greater chain breakage and mechanical properties degradation.

## 4. Conclusions

The recycling behavior of both 3 wt. % CNT-filled PC and neat PC were studied by repeated injection molding and granulating up to 20 runs. There was no significant change on the chemical structure of materials by FTIR. Results showed an overall decrease in the melt viscosity for both materials, the result of degradation of molecular weight. Compared to neat PC, there was a more pronounced change in melt viscosity of the CNT-filled PC, indicating lower resistance to degradation for the CNT-filled PC. Young's Modulus of both materials was little affected by recycling, however, other tensile properties including tensile strength, toughness and ductility of both materials decreased with recycling. Consistent with the rheology results, the CNT-filled PC showed a larger change in tensile strength, toughness, and ductility compared to the unfilled PC. The reduction in mechanical and rheology properties was attributed to chain scission and molecular weight reduction from the repeated high shear and thermal stresses in the recycling process. The overall higher melt viscosity of CNT-filled PC contributed to these higher stresses during recycling and the concomitant vulnerability to degradation during recycling. Breakage of CNTs by the high shear stresses may also be possible. The results show that for CNT-filled polymers more care in the recycling process is needed compared to the neat resins. The work is important to manufacturers using nanomaterials in these processes.

## 5. Acknowledgements

The researchers would like to acknowledge the support of the National Science Foundation (Award NSF-1120329).

## 6. **References**

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