

Investigating Environmental Weathering of CNF/CNT/ Thermoplastic Polymer Synthesized using Additive Manufacturing

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ABSTRACT

The stability of polymeric nanocomposites during the use phase and at the end-of-their useful life is not fully understood. The potential release of nanomaterials from polymer matrices becomes a concern as a high volume application of additive manufacturing is coming real. The degradation polymeric nanocomposites depends on the properties of the polymer and aging conditions. It is critically important to understand the relationship between the inherent characteristics of nanocomposite based consumer products and the likelihood of the release of nanomaterials throughout the life-cycle of the product. This research work is focused on weathering of additive manufacturing nanocomposites that contain different weight percentages of carbon nanofiber and carbon nanotubes. The weathering study was conducted using composites containing multi-walled carbon nanotubes (0 to 5 wt%) and carbon nanofiber (0 to 5 wt%). Various analytical techniques have been used for the characterization of structural changes and the potential for release of nanomaterials (NMs) from the composite matrix. Structural changes at selected times of the aging process were measured using thermogravimetric analysis and differential scanning calorimetry. These results are compared with weathered-nanocomposites that were manufactured by the conventional melt mixing techniques. Weathered materials were also characterized using FTIR, SEM and TEM and XRD, XPS, and AFM, to measure changes with increase aging. The release of CNT/CNF was analyzed using Single Particle- ICP-MS to detect metal catalysts releases that were used for the synthesis of CNF and CNT. The results of this study are essential to develop environmental risk assessment of additive manufactured materials over their life cycles.

Keywords: polymer weathering, additive manufacturing, nanorelease,

INTRODUCTION

Over the past decades the production and use of nanocomposite materials has been increasing rapidly. Many of these composites are used for outdoor applications, for example in automobiles, greenhouses, and for ropes. To meet these requirements, new polymers can be developed, or the current polymers can be modified to improve their properties such as mechanical stability, heat stability, barrier for water and air, fire retardant, optical and electrical properties. The incorporation of nano-fillers into crystalline or glassy state of the bulk samples will lead to significant change in the structure as well as morphology of the samples. At the same time, the mobility of the nano-fillers is much higher than that of the conventional composite fillers because of their comparable time scale of motion with the polymer chains. All of these factors contributed to a different energy dissipation mechanism of the bulk nanocomposites. However, it is found that the mobility of the polymer is a precondition for this mechanism to be effective and the increase in toughness in the presence of nano-particles scales with the increase in the mobility of the polymer chains. It is also why lots of samples functioning at their viscoelastic region usually would have more significant boost in properties.

Nanocomposites are materials made from a phases where one of more phases are at nanoscale. Unlike most engineering structure materials, the mechanical properties of micro-composites could vary as the direction along which measure changes that is they are isotropic. In order to change in chemical and physical properties of nanocomposites thermal analysis serves as a gross material characterization technique to determine chemical and structural changes of nanocomposites.

Additive manufacturing (*aka*, 3D printing) is an emerging technology for making a new class of multifunctional nanocomposites for many niche items such as medical implants, and a wide range of industrial designed components. Additive manufacturing technology allows printing complex 3D objects layer-by-layer enabling nanomaterials in new ways

toward greater control over material properties across three dimensions and could further extend capabilities of nanocomposites

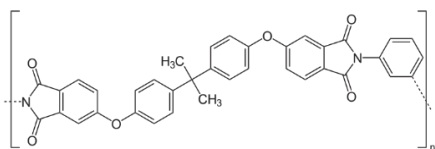
Energy, material use, and emissions during the manufacturing phase of composite materials are much higher than the amounts from the conventional materials. However, nanocomposite materials lighter and require much lower energy during the use phase. Life cycle risk assessment of nano composites includes the potential release of nanomaterials during manufacturing, use and end-of-life management (Figure 1). Polymers and nano-composites are increasingly used for structural applications such as boat and air craft construction, sporting goods and agricultural uses. There is often

The rate of deterioration of materials subjected to weathering depends on the nature of the materials. The concern regarding the durability of nano composites is partly because their relative newness but also because the changes during their useful lifetime and the potential impact of at the of their use. The objective of this study whether the deterioration of nanocomposite could release imbedded nanomaterials from the polymer matrix. Although there is a large volume of work on the hazard of nanomaterials, there are very limited studies on potential release of nanomaterials from composite matrix.

EXPERIMENTAL

Materials

The base polymer for this study is a ULTEM™ 1000, which is an amorphous, transparent polyetherimide (PEI) plastic offering a glass transition temperature (Tg) of 217°C. The high Tg makes the polymer to have high stability of physical and mechanical properties at elevated temperatures. PEI resins are used in medical and chemical instrumentation due to their heat resistance, solvent resistance and flame resistance. The composite samples were prepared using additive manufacturing (or 3D printing) technique with different amounts of CNT and CNF (Table 1).



Polyetherimide

Type	Wt CNF %	Wt CNT %	Wt Polymer %
A	5	1	94
B	5	2	93
C	5	3	92
D	5	4	91
E	5	5	90
F	0	10	90
E	10	0	90

Table 1: Types of Polyetherimide CNF/CNT composite tested

Accelerated aging of nano-composite

The flow of O₂ from the pressurized tank was controlled using mass flow controller (Sierra Instruments). The ozone generator was fed with up to 1L/min pure oxygen, and it can generate up to 2.5 g/hr of ozone in the oxygen stream. A tube furnace was provided to control the temperature of the reactor. The concentration of ozone was measured following the ozone generator with an ozone analyzer (Ozone Solutions). The concentrations of O₃ was analyzer were determined by the manufacturer's calibration for the ozone sensor. The gas flow to an ozone generator that has a capacity of up to 5 wt% conversion. Ozone-O₂ flow was bubbled through water before flowing into the tube furnace (Carbolite).

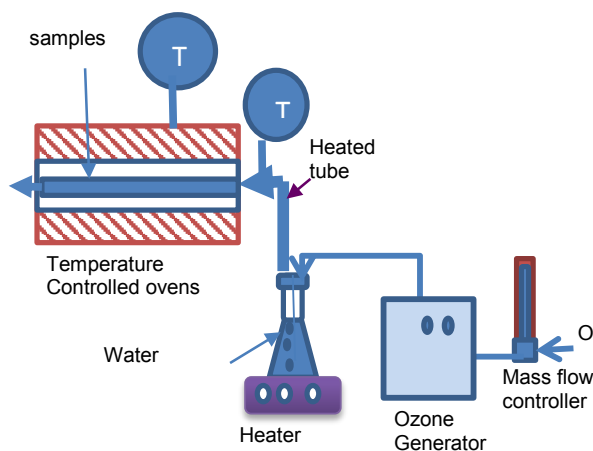


Figure 1: Schematic diagram of aging experimental setup

RESULTS

Microscopic observation

Microscopic observation of Ultem 1000/CNF/CNT composite before and after aging were compared. There were no surface cracks or other visible physical changes observed (Figure 2).

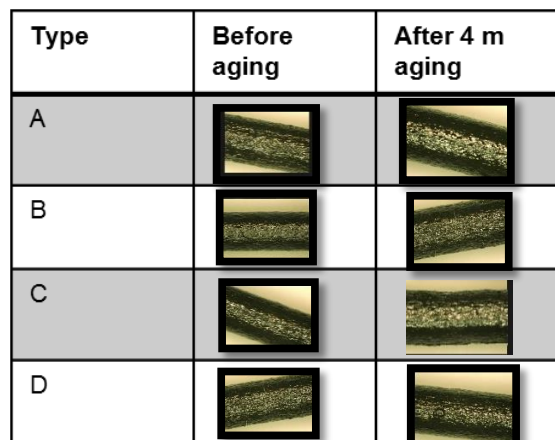


Table 2: Microscopic images of CNF/CNT composites

Thermogravimetric (TGA) Analysis of Weathered nanocomposite

TGA (Pyrus 1, PerkinElmer Cor.) is used in polymers for the determination of the thermal stability of polymers, compositional analysis, and identification of polymers from their decomposition pattern. The thermogram shown in Figure 2 illustrates weight losses of neat nanocomposite and ozone aged nanocomposites. Thermal analysis is a very simple technique for quantitatively analyzing for filler content of a polymer compound (e.g. CNT). The thermogram overlaps with the temperature range of hydrocarbon polymer degradation. The curves cannot be reliably deconvoluted since the actual decomposition range of a polymer in a polymer blend can be affected by the sample morphology. Results of thermogravimetric analysis weathered polymer samples (D) measured using PerkinElmer TGA7. TGA makes a continuous weighing of a small sample in a controlled atmosphere as the temperature is increased at linear.

The TGA data for sample D shows that PEI/CNT/CNF composite is stable up to 500 °C, above this temperature the polymer starts to degrade. There are three ways in which a polymer degrades: random scission, systematic chain scission or a combination of two. Random scission along the chain produces radicals or other reactive species. These reactive

species may continue to break down into progressively smaller species, which become volatile and are lost or they may attack other polymer chains leading to cross-linked polymers, which are less prone to degradation and ultimately lead to high temperature residue referred to as a char. The onset thermal decomposition temperatures were 550- 600°C. The thermal stability of the PEI/CNF/CNT decreased with oxidative aging. The stability of PEI composite decreased slightly from 576 °C to 547 °C for the extended exposure to ozone (Figure 2).

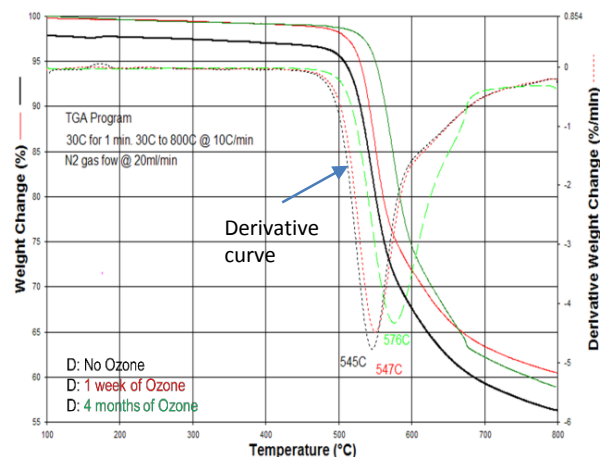


Figure 2: TGA of fresh and aged CNT/CNF polymer Composites

Fourier Transfer Infrared Spectroscopy Analysis

FTIR spectrum recorded using Cary 660 FTIR from Agilent Technologies Spectrophotometer. FTIR spectra for all samples were recorded by averaging 20 scans with 4 cm⁻¹ resolution. The FT-IR spectrum of the PEI is shown in Figure 1. It exhibits characteristic imide group absorptions at 1780 and 1720 cm⁻¹ (typical of imide carbonyl asymmetrical and symmetrical stretch), at 1355 and 743cm⁻¹ (C-N stretching and bending), and at 1234 cm⁻¹ (aromatic ether C-O-C) (Figure 3). The structural changes of weathered composites samples were evaluated by recording. Unfortunately no real evidence for amide and/or ester groups, no N-H clear-cut absorption band, could be detected on FTIR-ATR spectra because the neat and ozone exposed PEI/CNT/CNF spectra appear only differ slightly. This difficulty can be related to the similarity of the functional groups in both samples as well as to the FTIR-ATR technique itself. From the FTIR spectrum of weathered composites shows peaks around 2300 cm⁻¹ (Conjugated nitrile bond) gradually disappeared. This might be an indication of breaking of the polymer crosslinking breaking. t

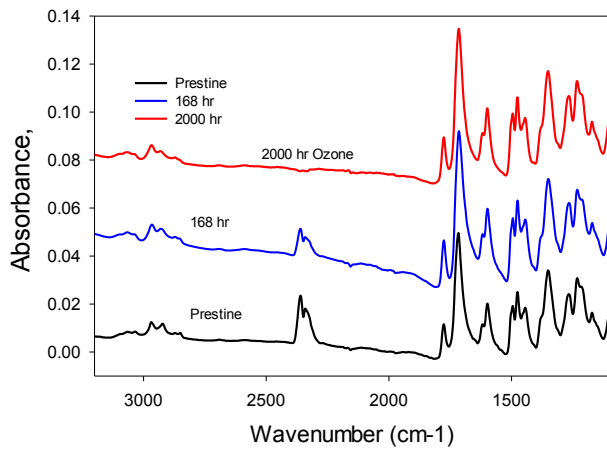


Figure 3. FT-IR spectrum of neat and ozone aged PEI/CNT/CNF

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