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Laser-induced thermo-oxidative degradation of carbon nanotube/polypropylene nanocomposites

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ABSTRACT

Nanocomposites of multi-walled carbon nanotubes and polypropylene were fabricated using twin screw extrusion and subjected to heating rates on the order of 100,000 degrees per second using laser pulse heating. Raman and infrared spectroscopy, as well as electron microscopy observations, showed that the nanotubes retain their structure and that a nanotube-rich layer formed at the surface of the composites during laser heating. By varying the weight fraction of filler in the composites, a 54% reduction in mass loss per laser pulse was achieved, compared to the pure polymer. The nanotube composites also displayed lower mass loss than nanoclay composites under the same conditions, despite having a significantly lower weight fraction of additive. Further reduction in mass loss per laser pulse was achieved in solvent-processed samples, which appear to have better dispersion than the extrusion-processed composites. We attribute these observations to the formation of a nanotube network formed on the surface, which acts as a protective barrier, slowing the degradation of the underlying polymer. Several observations made in this study are consistent with those reported in previously published slow heating rate studies, showing that while some phenomena are unique to transient heating, there are some commonalities between the two regimes.

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1. Introduction

Organic-based polymers are increasingly being used to replace inorganic materials in some applications where the material may be subjected to elevated temperatures. Since most polymers have a relatively low melting and thermal stability temperature compared to materials like metals and ceramics, the addition of particles to the polymer matrix is often needed to produce a composite with improved thermal stability. There has been a substantial amount of research on the use of nanoparticles as additives to polymers to improve both the mechanical and thermal properties. Fillers such as nanoclay and carbon nanotubes have been among the most widely investigated for many years [1–3]. Carbon nanotubes are high aspect ratio carbon nanostructures that may be thought of qualitatively as graphene layers that have been rolled into a tubular shape. Carbon nanotubes exhibit extremely high strength, modulus, and thermal and electrical conductivity, and when dispersed well in a polymer matrix, can form a network structure throughout the composite.

The thermal stability or flammability of carbon nanotube nanocomposites has been studied previously [4,5]. In traditional thermal stability studies, the nanocomposite is heated at rates on the order of 10 °C/min. Using thermogravimetric analysis (TGA), the mass change of the sample is recorded and the thermal stability is determined as a measure of the mass loss versus temperature. The thermal degradation of the nanocomposite can be determined under both oxidative and non-oxidative conditions. Kashiwagi et al. [6,7] showed that 1 and 2 vol% multi-walled carbon nanotubes (MWCNT) in polypropylene increased the thermal stability of the polymer during TGA tests in air and nitrogen, and decreased the heat release rate in a cone calorimeter and gasification tests. The high aspect ratio carbon nanotubes formed a networked structure covering the sample surface, acting as a thermal shield and slowing the degradation of the underlying polymer. Incorporation of MWCNTs into other polymer materials has shown similar behavior [8–10]. It has been shown that effective dispersion of the nanotubes in the polymer matrix is critical for the reduction

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in mass loss rate during flammability tests [11]. Well-dispersed nanotubes form a homogeneous network layer, whereas poorly dispersed nanotubes form a discontinuous layer consisting of fragmented islands of networked nanotubes on the composite surface. Well-dispersed nanotubes also lead to a higher viscosity of the polymer melt, making bubble formation and coalescence more difficult. Decreased bubbling and bursting leads to a nanotube network layer that is more intact. This continuous protective network layer leads to improved fire retardance. Carbon nanotubes have also been shown to provide superior enhancement to fire retardance compared to other carbon nanoadditives, such as carbon nanofibers and carbon black [5].

Certain applications, such as ballistic environments, have heating rates that are many orders of magnitude larger than those typically achievable in thermogravimetric analysis or flammability studies, necessitating the use of alternative methodologies to study such regimes. Laser pulse heating (LPH) has been used to achieve heating rates on the order of 10^7 K/min [12–14]. In order to achieve photothermal heating and to avoid photochemical effects (as seen with the use of UV wavelength lasers), an infrared laser with variable pulse duration on the order of milliseconds is used to heat the sample surface. By adding the same weight percentage of carbon black to each of the composites, uniform optical absorption of the laser light among samples of various compositions can be achieved [15,16]. Studying the thermal degradation of polymer nanocomposites with this method combines phenomena seen in both polymer ablation and polymer thermal stability/flammability research. We can observe ablation of material, melting and bubbling of the heated polymer, and degradation of the polymer chains. This group has previously studied highly transient heating of polymer/nanoclay nanocomposites [17] and observed decreased mass loss with increasing amounts of montmorillonite nanoclay in a polypropylene matrix. Spectroscopic characterization showed that a silicate-rich layer forms on the surface of the LPH region of the composite, providing a mechanism of protection for the underlying polymer. While carbon nanotube composites have been studied at slow heating rates, they have not been studied at high heating rates. The objective of this study is to determine how carbon nanotube/polymer composites behave under highly transient heating and whether correlations can be made to the behaviors observed during low-heating rate thermal stability and flammability testing.

2. Experimental

2.1. Composite preparation

Isotactic Polypropylene (PP) pellets (Total Petrochemical Type 3371, MFR = 2.8 g/10 min at 230 °C, 2.16 kg) were dried for 16 h under vacuum at room temperature. A master batch (Nanocyl PP2001CNT/Thermoplastic) at 20 wt% MWCNTs (with average 9.5 nm diameter and 1.5 μm length) were compounded with appropriate amounts of the neat PP resin to achieve desired final loadings using a co-rotating twin screw extruder and a controlled feeder. Zone 1 was held at 170 °C and zones 2–4 and the die were held at 220 °C and screw speed at 200 RPM. Pellets were extruded through a 1/16″ circular die and passed through an ice bath prior to being pelletized. They were then passed through the extruder for a second time under identical conditions. Using electrical conduction as a measurement for MWCNT dispersion, it was found that two sequential passes through the extruder (under identical conditions) improved dispersion. Additional passes through the extruder yielded increased conductivity up to five passes, though physical properties did not show a corresponding increase beyond two passes. For this reason (as well as additional processing time), the compounding step was limited to two passes. Composites were made with 0.5, 1.0, 2.0, 3.0 and 5.0 wt% MWCNT.

Compounded PP/MWCNT pellets were melt-pressed at 200 °C in a steel die with PTFE release film. No pressure was applied for 5 min while the melt press equilibrated and the PP began to melt/flow. Pressure was then applied in 13.7 MPa increments to 68.9 MPa. The pellets were left under 68.9 MPa for 300 s, at which time they were removed and cooled to room temperature. The newly-formed discs were removed from the die and any flash material was trimmed from the edges. All materials were compounded with 1 wt% carbon black (Cabot, Monarch 120) to give the materials uniform optical absorption during laser irradiation.

For comparison with the 1 and 2 wt% MWCNT composites fabricated by extrusion, samples of the same weight loading of nanotubes were fabricated by a solvent processing method. MWCNTs (NanoLab PD15L5-20) were horn sonicated (Cole-Parmer VCX-500) at 20% amplitude for 45 min in p-xylene (ACROS CAS #106-42-3) with 1% Triton X-100 (ACROS CAS #9002-93-1) surfactant. In this case, the nanotubes are nominally 15 nm in diameter and 5–20 μm in length. The mixture was heated on a hot plate to
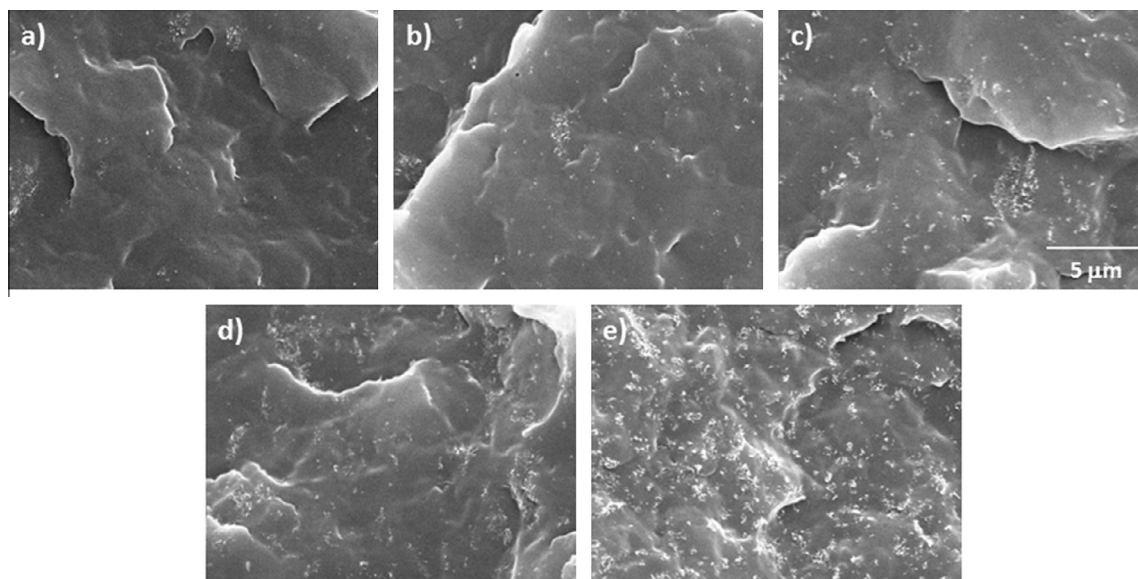

Fig. 1. The dispersion of MWCNTs in the polypropylene matrix as seen in the cross sections of cryo-fractured samples for (a) 0.5, (b) 1.0, (c) 2.0, (d) 3.0, and (e) 5.0 wt% MWCNT composites.