



Thermal stability of polypropylene-clay nanocomposites subjected to laser pulse heating



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ABSTRACT

Polypropylene based nanocomposites filled with montmorillonite nanoclay prepared by twin screw extrusion have been studied for thermal stability at high heating rates. In contrast to traditional thermal stability and flammability studies of polymer nanocomposites using heating rates on the order of tens of degrees per minute, this study achieves heating rates that are six orders of magnitude higher. This was accomplished using laser pulse heating. The results show that the nanoclay increases thermal stability of the polymer, as measured by a decrease in the mass loss of a laser pulse at a given energy and intensity. Electron microscopy and various spectroscopic techniques show that a silicate-rich char layer may provide the mechanism for protection of the polymer and decreased degradation rates. The results of the study are compared to the typical results found in traditional thermal stability testing.

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1. Introduction

The addition of nanoscale material to polymer matrices for improved mechanical, thermal, and electrical properties has been studied extensively in recent years [1–3]. One of these nanoscale materials, montmorillonite (MMT), is a layered-aluminosilicate clay consisting of silicon dioxide tetrahedral layers with a metal oxide octahedral center layer [4]. The nanoclay has plate-like morphology with a thickness on the order of 1 nm and in-plane dimensions on the order of several hundred nanometers. Naturally hydrophilic, the nanoclay must be organically modified in order to be dispersed into a hydrophobic polymer. This is typically accomplished by substituting the sodium counter ions with, for example, an organic quaternary ammonium ion that contains alkyl chains. Van der Waals or hydrogen bonding is responsible for holding the clay platelets together, which allows the plates to easily expand or contract dependent upon the cation that is exchanged between the plates. The *d*-spacing of the clay platelets is easily measured by X-ray diffraction (XRD) and can give information on the intercalative state of the clay. Layered-silicate nanoclay can be dispersed

into polymers using melt-mixing techniques [5,6]. Well-dispersed and exfoliated clay can provide improved properties for the polymer, such as increased thermal stability.

The thermal stability of a polymer is measured as the resistance to weight loss and chemical change, or degradation, when exposed to higher temperatures. The analytical technique conventionally used for characterizing thermal stability is thermogravimetric analysis (TGA), where the mass of the sample is monitored as the temperature increases. Thermal stability tests have traditionally been performed under relatively slow heating conditions, at heating rates on the order of 20 °C/min or below, while some equipment is able to reach heating rates about one order of magnitude higher.

Many studies have shown that the addition of nanoclay into polymer matrices generally increases the thermal stability of a polymer during TGA characterization [7–12]. Qin et al. demonstrated that a 5 wt% organically modified montmorillonite addition to polypropylene can increase the temperature at which the peak degradation rate occurs by about 50 °C compared to the pure polymer when heated at 20 °C/min in air [8]. In addition to thermal stability testing by TGA, several groups have conducted research on the flammability properties of polymer-nanoclay composites [13–18]. In work by Gilman et al., polypropylene (PP)-layered silicate nanocomposites had a 75% lower peak heat release rate, HRR,

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compared to the pure polymer during cone calorimetry testing [13]. The enhanced thermal stability and flammability resistance of the nanoclay-polymer composites is attributed to the formation of a protective char layer in the nanocomposite, a multilayered carbonaceous-silicate structure that acts as an excellent mass transport barrier, slowing the flow of heat into the polymer and slowing the escape of the volatile decomposition products from the polymer [14].

While these testing methods provide information on the behavior of polymer nanocomposite during slow heating rate regimes, they are inadequate in describing how the material behaves during extremely high heating rates that may be of interest in applications such as ballistic environments [19]. The application of laser pulse heating (LPH) with a variable pulse duration millisecond laser opens a new regime of study on these materials at heating rates up to six orders of magnitude higher than those achievable with conventional methods. There is literature precedent for investigating the degradation of polymers (simulating rapid heating during severe fires) using laser heating [20–23]. Here, we attempt to extend this work to the case of polymer nanocomposites, using a millisecond pulsed laser.

2. Experimental

2.1. Preparation of the nanocomposites

The clay nanocomposites were prepared by mixing in a twin screw extruder at 100 rpm. Zones 1 through 4 of the extruder were at 150 °C, 190 °C, 190 °C, 190 °C, respectively and the die was at 190 °C. The extrudate was subsequently passed through an ice water bath before being pelletized. The pellets were stored under vacuum at elevated temperature (40 °C) overnight to remove any residual moisture. Dried pellets were then fed into a single screw extruder (Zone 1–170 °C, Zone 2–180 °C and Zone 3–180 °C) and extruded through a circular die for the sole purpose of forming a rod shape of a desired diameter unavailable to us with the twin screw dies. The rod was then machined into slices approximately 2 mm thick for laser pulse heating experiments. Pure isotactic polypropylene (Fortilene, Melt Flow Index of 2.8 g/10 min, at 230 °C and 2.16 kg) was used to let-down the clay masterbatch. The clay masterbatch (Nanocor, NanoMax-PP) contained 50 wt% organically modified (quaternary ammonium) Montmorillonite (MMT) clay with compatibilizers, grafted maleic anhydride (PP-g-MA). The polypropylene used in the masterbatch has a Melt Flow Index of 20 g/10 min, according to the manufacturer. All material included 1 wt% carbon black (Cabot, Monarch 120) to give the materials uniform optical absorption during laser irradiation. Pure polypropylene (PP-0), PP with 5 wt% MMT (PP-5), 10 wt% MMT (PP-10), 25 wt% MMT (PP-25) and 50 wt% MMT (PP-50) samples were prepared for this study.

2.2. Laser pulse heating

The Laser Pulse Heating (LPH) setup included an Nd:YAG laser (MegaWatt Lasers, Inc) that sends 1064 nm light into an optical fiber. The light from the fiber was passed through a 50 mm focal length collimating lens, followed by a 250 mm focal length objective lens, which produced a laser spot diameter of 3.0 mm (0.003 m). The incident laser energy was measured using a beam splitter (Newport) and an energy meter (Ophir Nova). The laser pulse energy and pulse duration can be adjusted, but all samples in this paper were irradiated at 3.1 J pulses lasting 5 ms, corresponding to a fluence of 44 J/cm² and an intensity of 8.8 kW/cm². The samples were irradiated in air to give thermo-oxidative conditions. The reflectance of the samples was measured in a UV–vis spectrometer (Perkin–Elmer Lambda 40) at 1064 nm and found to

be approximately $8 \pm 0.2\%$, meaning most of the laser light was absorbed into the sample, as desired.

2.3. Characterization of nanocomposites

The mass of the sample was weighed before and after irradiation on a microbalance with a readability of ± 0.001 mg (Sartorius ME-36 S). Ten samples for each condition were run for statistics. Scanning Electron Microscopy (SEM) was performed on a JEOL-840 electron microscope operating at 10 kV equipped with Energy Dispersive Spectroscopy (EDS) with a Thermo Electron 457A X-ray detector, and an FEI Helios Nanolab 600i Field Emission Electron Microscope (FE-SEM) operating at 5 kV. Samples were coated with a thin layer of gold in order to reduced charging effects. Fourier Transform Infrared Spectroscopy (FTIR) was performed on a Perkin–Elmer Spectrum One Spectrometer operating in Attenuated Total Reflectance mode (ATR) between 4000 cm⁻¹ to 515 cm⁻¹ at 4 cm⁻¹ resolution. X-ray Photoelectron Spectroscopy (XPS) was conducted on a PHI5701 LSci with a monochromated Al-K α 1486.6 eV X-ray source (Evans Analytical Group). X-ray diffraction (XRD) was performed on a Bruker D8 Discover diffractometer with Cu-K α radiation ($\lambda = 1.505945$ Å) from 5 to 25° 2θ with a 240 s accumulation time. The distance, between clay sheets, d , was calculated by Bragg's Law, $n\lambda = 2d \sin \theta$, using 2θ peaks from the XRD spectra. Transmission Electron Microscopy (TEM) samples were prepared by carefully removing char material from the surface of a LPH region of the nanocomposite under a microscope using ultrafine tweezers. The material was deposited onto a carbon coated Cu TEM grid for viewing on an FEI Titan Environmental S/TEM operating at 300 kV. Profilometry of LPH samples was conducted on a Nanovea ST400 non-contact optical profilometer. The total ablated volume, as defined by the material loss below the initial sample, and the volume above the original surface, was determined by 3-D surface topography.

3. Results and discussion

3.1. Mass loss measurements

Clay nanocomposites with varying clay content were subjected to conventional TGA and LPH. The TGA results confirmed the behavior expected from the literature, namely, increasing clay content leads to increased thermal stability for a fixed heating rate. The results of the TGA are similar to those published previously in the literature [7,8]. The mass loss for each clay nanocomposite during LPH is presented in Fig. 1. Error bars on the mass loss data

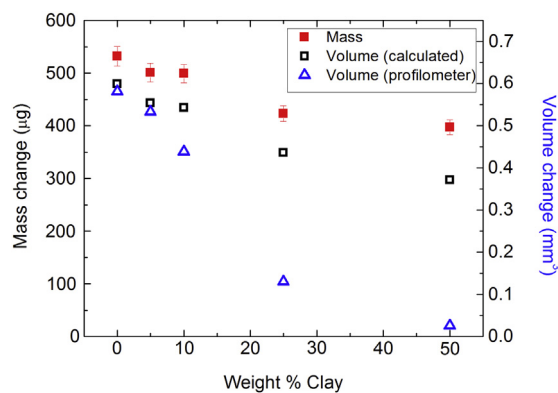


Fig. 1. Mass loss and volume loss of nanoclay composite material after laser pulse heating with a fluence of 44 J/cm² (8.8 kW/cm², 3.1 J, 5 ms) (average of 10 samples per data point).

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