

Supporting information

Catalyzing carbonization of polypropylene itself by supported nickel catalyst during combustion of polypropylene/clay nanocomposite for improving fire retardancy

Tao Tang,^{a,*} Xuecheng Chen,^{a,b} Hui Chen,^a Xiaoyu Meng,^a Zhiwei Jiang,^a Wuguo Bi^a

a. State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

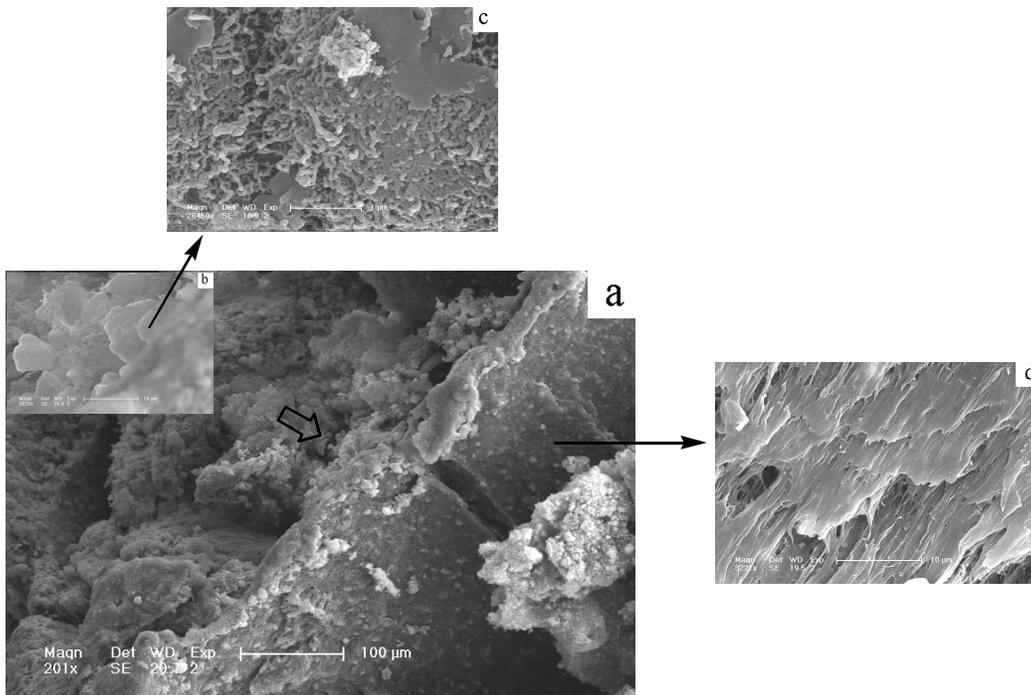
b. Department of Chemistry, Shanghai University, Shanghai 200436, China

Materials and Preparation of nanocomposites Polypropylene (PP, melt flow index of 0.8 g/min), was mixed with organic-modified clay (OMC, Cloisite 15A from Southern Clay, organic modifier: dimethyl-dihydrogenatedtallow quaternary ammonium; modifier concentration: 125meq/100g clay) and/or supported nickel catalyst (Ni-Cat, nickel supported on silica-alumina, Ni content \approx 66%, from Alfa Aesar) in a Brabender mixer at 100 rpm and 190 °C for 10 minutes. Maleated polypropylene (PP-MA, acid value 26 mg KOH/g), 5 wt%, was added into the above mixture as a compatibilizer. In order to observe char formation during combustion, a piece of the above nanocomposite was put into a crucible, heated at the bottom to 700°C until not flame anymore; the charred residue was cooled to room temperature and weighed. Subsequently, the charred residue was purified with hydrofluoric acid and nitric acid to eliminate OMC, amorphous carbon and most of Ni-Cat. The yield of the residue (y_1) is calculated by amount of the residue (m_1) divided by amount of the nanocomposite (m_0), i.e., $y_1 = (m_1/m_0) \times 100\%$. The yield of the purified char (y_2) is calculated by amount of the purified char (m_2) divided by amount of the PP in the used nanocomposites (m_0), i.e., $y_2 = (m_2/m_0) \times 100\%$. All of the samples were weighed by analytical balance.

Characterization Evaluation of flammability was achieved using a Cone Calorimeter (Fire Testing

Technology). The tests were performed at an incident heat flux of 35 kW/m^2 in accordance with ASTM E 1354. All measurements were done in triplication.

Scanning electron microscope (XL30EsEM FEG field emission microscope operated using 20kV voltage) and transmission electron microscope (JEM-2010, operated at 200 kV voltage) were used to characterize the morphology and microstructure of the nanocomposite and its residual char. The nanocomposite was ultramicrotomed with a diamond knife at room temperature to give 70 nm thick sections. The microstructure of the nanocomposite which was burned shortly at 700°C to imitate the combustion environment of the cone calorimeter was observed by means of Field emission SEM (SFigure 1). The sample was cut into two parts. There were two zones, one of them was the charred residue and another was the nanocomposite. In the charred residue, a lot of nanofiber-like charring material intermingled with clay layers appeared. The results showed that PP was retained in the system during combustion.



SFigure 1 FE-SEM micrographs of the cut surface of PP nanocomposite containing Ni-Cat burned partly. a) the cut surface of the nanocomposite; b) and c) microstructures of the external combusted residue; d)

microstructures of the inner nanocomposite.

The purity and phase structure of the products were obtained by X-ray powder diffraction (XRD) using a Rigaku D/MAX-IIIB powder X-ray diffractometer with Cu K α radiation. From X-ray powder diffraction (XRD) patterns of the PP/PP-MA/OMC/Ni-Cat composites, the XRD peaks from the OMC are found at angles lower than 10°, inferring the intercalated structure of PCM-08 in Table 1. The diffraction peaks of PP and OMC in the charred residue disappeared completely after burning, and those of Ni-Cat remained. Meanwhile two new diffraction peaks appeared, one ascribed to the clay without surfactants and the other to carbon materials with graphitic structure. The charred residue was purified with nitric acid and hydrofluoric acid to remove amorphous carbon, the clay and most of the Ni-Cat, except part of the Ni-Cat enwrapped by carbon nanotubes. Then there only appeared a small hump and a strong diffraction peak at 25.7° coinciding approximately with that of (002) diffraction of graphite.

Raman spectroscopy (T6400, excitation beam wavelength: 514.5 nm) was used to characterize the vibrational properties of the purified char from PCM-08 (Table 1), graphite and commercial multi-walled carbon nanotubes (MWNT). There are two vibrational peaks on the Raman spectra of the above samples. Furthermore, Raman spectrum of the purified char is similar to that of the commercial MWNTs. For Raman spectra of MWNTs, the peak at 1585 cm⁻¹ (G-band) corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp₂-bonded carbon atoms in a graphite layer, and the D-band at about 1353 cm⁻¹ is associated with vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons. Similarly, for Raman spectra of the purified char, the peak at 1599 cm⁻¹ (G-band) also corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp₂-bonded carbon atoms in a graphite layer, and the D-band at about 1353 cm⁻¹ is associated with vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons.