



Research paper

Preparation and properties of halogen-free flame-retardant layered silicate-polyamide 66 nanocomposites

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ABSTRACT

The relationship between the morphology, flammability and mechanical properties of layered silicate-polyamide 66 (PA66) nanocomposites was investigated. The nanocomposites were composed of PA66, melamine-modified layered silicate (MLS) as a nanofiller, and/or melamine cyanurate (MC). Samples of MLS with different dispersion states were obtained by changing the melt-mixing procedures for PA66, MLS and MC. X-ray diffraction (XRD), transmission electron microscopy (TEM), thermal analysis, strength tests, cone calorimetry tests and UL 94 vertical burning tests were used to examine the effects of MLS on the morphology, mechanical properties and flame resistance performance of the materials. The data revealed a correlation between the dispersion state of the MLS layers and flame retardancy. The nanocomposite manufactured by one-stage kneading of a mixture of PA66, MLS and MC earned a UL 94 rating of V0. The flame retardancy of dripping particles during combustion was found to be due to uneven dispersion of MLS in the PA66 matrix.

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1. Introduction

PA66 is an engineering thermoplastic with superior thermal and mechanical properties, strong chemical and electrical resistance, and durability against fatigue and abrasion. PA66 is used in the manufacture of fibers and automotive and electrical parts; its wide use in the manufacture of electrical parts is due to its self-extinguishing characteristics. Extending the flame retardancy of PA66 would likely augment its rigidity and heat resistance (Urabe and Morimoto, 2005; Yamamoto and Negi, 2008; Hesse et al., 2011). Recently, growing environmental awareness has underscored the global demand for flame-retardant polymers that are environmentally friendly yet deliver superior flame resistance, without any loss of performance.

Environmental concerns have focused attention on non-halogen techniques for producing flame-retardant plastics. Alternatives to traditional halogen-free flame retardants include metal hydroxides, red phosphorus, organophosphorus compounds, and ammonium polyphosphate (Jeng et al., 2002; Pecht and Deng, 2006; Hornsby, 2007; Feng et al., 2013), but the use of relatively benign nanocomposites using silica or clay minerals in particular merits investigation (Gilman et al., 1997, 2000; Hu et al., 2003; Zammarano et al., 2005; Morgan, 2006; Fang et al., 2009, 2011; Isitman et al., 2009; Laoutid et al., 2009; Shi et al., 2009; Tsai et al., 2010; Charalampos et al., 2011; Ito et al., 2011; Huang et al., 2011; Orhan et al., 2012; Rathi and Dahiya, 2012;

Samyn and Bourbigot, 2012, 2014; Lorenzetti et al., 2013; Batistella et al., 2016). Clay-polymer nanocomposites (CPN) are formed by the exfoliation of clay layers, develop flame retardancy without the need to incorporate other flame retardants, and often exhibit remarkably improved rigidity, heat resistance, and barrier properties (Tamura et al., 2009; Uno et al., 2009). These properties are strongly affected by the interaction between the clay surface and the polymer, the aspect ratio, and the dispersion state of the clay particles, among other factors. When the CPN burns, the dispersed nanoparticles in the polymers form a surface char layer. Further research into CPN is highly warranted because they suppress flammability without the use of large quantities of flame retardant.

The UL 94 flame tests are a family of flammability standards developed by Underwriters Laboratories in the USA and are used to establish the flammability of plastic and other materials used to manufacture parts for devices and appliances. Plastics are classified according to how they burn in various orientations and at different thicknesses. The key acceptance criterion is quick and/or efficient extinguishing of the flame on the burning specimen. Each plastic electronic component must pass a UL 94 test, typically by earning the UL 94 V0 rating. There have been few reports of simple CPN systems attaining this rating. In one such report, Fang et al. (2011) described the intumescent flame retardation of CPN consisting of polyamide 6 (PA6), melamine-modified montmorillonite, and melamine pyrophosphate (MPP); a 3 mm thick sheet of a flame-retardant material comprising a blend of 23 mass% MPP with 1–2 mass% of clay achieved V0 flame retardancy. However, the amount of halogen-free flame retardant generally must be higher

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than this to provide a practical flame retardant material. It is therefore important to improve the mechanical properties and moldability of the material. In parallel with this is the urgent need for halogen-free flame retardant materials that meet the UL 94 V0 standard when tested as very thin coatings. These materials are required as flame retardant coatings for electric/electronic parts that are exposed to high temperatures or high voltages, such as connectors, contactors, motor insulators and molded case circuit breakers.

Melamine is a triazine compound commonly used as a flame retardant and was used in this study as an intercalant in layered silicates. The intent of this study was to control the balance between flame resistance and other characteristics of the layered silicate material by using as few flame retardants as possible, and at the same time to develop a PA66 based CPN that exhibits high stiffness, and halogen-free flame retardancy. A small amount of melamine cyanurate was used as a flammability synergist. Flame resistance experiments were performed to characterize conformance to the UL 94 standard, and standard tensile strength and flexural modulus analyses were performed to assess mechanical properties.

2. Experimental

2.1. Materials

PA66 (Technyl® A216, Rhodia) is a matrix polymer with a relative viscosity of 2.61 (in H₂SO₄), as determined according to International Organization for Standardization (ISO) 1874-1. Melamine was purchased from Nacalai Tesque, Inc. The layered silicate (LS) was a synthetic expandable fluoromica (ME100) with the chemical composition Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96} (Tateyama et al., 1997), had a cation exchange capacity (CEC) of 89.4 meq/100 g, and was provided by CO-OP Chemicals, Tokyo, Japan. The “typical flame retardant” melamine cyanurate, MC (MC6000) was supplied by Nissan Chemical Industries, Ltd.

2.2. Sample preparation

Melamine hydrochloride salt was prepared from melamine and hydrochloric acid, then melamine-modified layered silicate (MLS) was prepared by a cation exchange reaction between ME100 and melamine hydrochloride salt at 60 °C for 3 h. The product was collected by filtration and washed several times with a mixture of distilled water and ethanol, then dried at 80 °C overnight to remove water.

CPN were produced by melt-mixing at 270 °C using a twin-screw extruder (PCM30, Ikegai). The compounding procedure includes one- and a two-stage kneading process that allows fine control of the MLS dispersion process. In one-stage kneading, the raw materials are placed together in the kneader. In two-stage kneading, a 10 mass% MLS master batch (Mb) is first produced by mixing and kneading PA66 pellets with MLS, then the final compound is produced by mixing and kneading the Mb and MC, using PA66 as a diluent. The formulation ratios of the samples (S-1, S-2 and S-3) are shown in Table 1. Extruded pellets were dried and injection-molded into standard tensile, flexural tests, heat distortion temperature (HDT) and Izod specimens using an injection molding machine (IS80G, Toshiba Machine Co., Ltd.). The amount

of silicate in each extruded batch was determined by placing pre-dried pellets in a furnace at 600 °C for 4 h and weighing the residual ash.

2.3. Characterization

Samples were subjected to X-ray diffraction (XRD) measurements (Ultima IV, Rigaku) using CuK α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA with a scan rate of 2° min⁻¹. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Thermoplus TG8120, Rigaku) under an airflow at a uniform heating rate of 10 °C/min up to 1000 °C. Fourier transform infrared (FTIR) spectra were obtained using an attenuated total reflectance (ATR)-FTIR spectrometer (IR Affinity, Shimadzu) on a diamond crystal from 400 to 4000 cm⁻¹. Transmission electron microscopy (TEM) experiments were conducted on samples extracted from the core region of tensile specimens. Details of the layer morphology were investigated by preparing ultra-thin cross-sections of these materials using a focused ion beam microscope (Xvision 200DB, SII NanoTechnology). The resulting sections were viewed under a JEM 1010 microscope (Jeol) operating at 100 kV.

An injection molding machine (IS80G, Toshiba Machine) was used to injection-mold the extruded pellets into ISO multipurpose test specimens. The specimens were shaped like a tensile dog-bone sample 170 mm long and the center section was 10 mm wide by 4 mm thick by 80 mm long. The injection molding parameters were a cylinder temperature of 270 °C and a mold temperature of 40 °C. Test pieces for the flexural, heat distortion temperature (HDT) and Izod tests were 80 mm × 10 mm × 4 mm cuboids. The specific gravities of the samples were estimated using a densimeter (SD200L, Ektron Tek) according to American Society for Testing and Materials (ASTM) D792. Standard tensile, flexural, HDT and Izod impact strength values of PA66 and its CPN were determined according to ISO 527-1, ISO 178, ISO 75-1 and ISO 180, respectively. After molding and/or cutting, the specimens were immediately sealed in aluminum bags and placed in a temperature-controlled room (23 °C) for 24 h prior to mechanical testing. The reported values are averages of five individual measurements.

Vertical burning tests were conducted according to UL 94 on 125 mm × 13 mm × 0.5 mm³ sheet samples prepared using a test press. The morphologies of the char residues were observed using a scanning electron microscope (JSM-6700FT, Jeol) at 7 kV. Cone calorimetry tests were conducted following the procedures in ISO 5660 using a cone calorimeter (Cone III, Toyo Seiki). All samples (100 mm × 100 mm × 2 mm³) were exposed horizontally to an external heat flux of 50 kW/m².

3. Results and discussion

3.1. CPN morphology

XRD patterns for pristine layered silicate (LS) and melamine-modified layered silicate (MLS) are shown in Fig. 1. The value of $2\theta = 7.2^\circ$ in LS shifted to $2\theta = 7.0^\circ$ in MLS due to the intercalation of melamine molecules, which also increased the interlayer distance from 1.23 to 1.27 nm. This increase in distance suggests that the melamine rings were intercalated in a parallel fashion between each layer (Fig. 1, inset). The intercalated melamine content was estimated to be 12 mass% based on the total mass loss from 150 to 1000 °C in TG measurements.

X-ray patterns for CPN made from the three types of compound (S-1, S-2, and S-3) are presented in Fig. 2. Simple addition of MLS to the PA66 matrix, as shown in curve (a), gave broad and faint shoulder reflections that replaced the 1.27 nm reflection. The finite layer expansion (1.27 nm) associated with an intercalated structure (MLS) resulted in the disappearance of a basal reflection that corresponded to the exfoliating clay mineral layers. The XRD patterns changed significantly when the conditions under which the samples were prepared were changed. As opposed to S-1, which had no reflections (curve a), samples S-2 and S-3 (curves b and c) showed two reflections at around $2\theta =$

Table 1
Kneading process and formulation ratios for each sample.

Sample	Process	Feed materials	Composition (mass%)
S-1	One stage kneading	PA66 + MLS	PA66/MLS (95/5)
S-2	Two stage kneading	(1st) PA66 + MLS 10%	PA66/MLS (90/10)
		(2nd) Mb + PA66 + MC	PA66/MLS/MC (93/3/4)
S-3	One stage kneading	PA66 + MLS + MC	PA66/MLS/MC (93/3/4)

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