Thermochimica Acta 495 (2009) 63–71

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The effects of intralayer metal composition of layered double hydroxides on glass transition, dispersion, thermal and fire properties of their PMMA nanocomposites

Charles Manzi-Nshuti [a], Dan Chen [b], Shengpei Su [b], Charles A. Wilkie [a,*]

[a] Department of Chemistry and Fire Retardant Research Facility, Marquette University, Milwaukee, WI 53201-1881, USA
[b] College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, People's Republic of China

ARTICLE INFO

Article history:
Received 30 March 2009
Received in revised form 29 May 2009
Accepted 4 June 2009
Available online 12 June 2009

Keywords:
Nanocomposites
Fire retardancy
Thermal analysis
Cone calorimetry

ABSTRACT

A series of aluminum-containing layered double hydroxides (LDHs), containing Mg, Ca, Co, Ni, Cu and Zn as the divalent metals, have been prepared by the co-precipitation method and used to prepare nanocomposites of PMMA by *in situ* bulk polymerization. The additives were characterized by Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy (XRD) and thermogravimetric analysis while the polymer composites were characterized by XRD, transmission electron microscopy, differential scanning calorimetry and cone calorimetry. Polymerization of methyl methacrylate in the presence of these undecenoate LDHs results in composites with enhanced thermal stability. The glass transition temperatures of the composites and the pristine polymers are found to be around 110 °C; this suggests that the presence of these additives has little effect on the polymer. It is found that the additive composition and the dispersion state of LDHs agglomerates in the polymer matrix influence the fire properties of composites as measured by cone calorimetry.

1. Introduction

Recently, clay/polymer nanocomposites have attracted considerable interest as the clays are used as reinforcements of polymeric materials [1–3]. Clay/polymer nanocomposites often have properties that are dramatically different from those of the polymer alone with unique improvements in mechanical strength [4], thermal stability [5], flammability [6] and gas permeability [7]. The compatibility of the clay between the polymer and the clay is crucial for the formation of well-dispersed nanocomposites [6].

Until now, however, the work on polymer/clay systems have mainly focused on montmorillonite-type layered silicate whose layers have a relatively low charge density and from which montmorillonite-type layered silicate/polymer nanocomposites can be easily obtained [8–11]. Recently, there has been a growing interest in the preparation of other layered nanomaterials, like the layered double hydroxides (LDHs).

LDHs or hydrotalcite-like materials [12–14] are a class of anionic clays whose general formula is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}{}^{n-}\cdot mH_2O]^{x-}$, where M(II) and M(III) represent divalent and trivalent metal cations, respectively. The interlayer anion (A^{n-}) may be varied over a wide range and the value of the stoichiometric coefficient (x) should be between 0.2 and 0.33 [15].

Poly(methyl methacrylate) (PMMA) is an optically clear amorphous thermoplastic. It is widely used as a substitute for inorganic glass, because it shows higher impact strength and undergoes ductile rather than brittle fracture. It has favorable processing conditions, and a wide range of additives have been shown to further improve its properties [16].

Wang et al. prepared disorderly exfoliated LDHs/PMMA nanocomposites by *in situ* polymerization and observed enhancement of the decomposition temperatures and the glass transition temperature compared to pristine PMMA [17]. Bao et al. reported an enhancement in tensile strength, Young's modulus, and an increase of the glass transition temperature of the PVC/LDH nanocomposites relative to those of pristine PVC [18].

Qu et al. successfully synthesized exfoliated LDHs/PE-g-MA [19] and LDHs/LLDPE [20] nanocomposites by refluxing the LDH in a xylene solution of PE-g-MA and LLDPE, respectively. In earlier work from this laboratory [21], undecenoate-LDHs of ZnAl, CoAl and NiAl were found to greatly enhance the thermal stability of melt blended PMMA while the cobalt-rich LDH at 10% loading in PMMA gave a 41% reduction in peak heat release rate (PHRR) relative to the pristine polymer. Also, good dispersion and enhancement of both fire and thermal properties were obtained for a combination of a series of alkyl carboxylate-modified LDHs with PMMA [22]. The initial work on using LDHs to enhance fire retardancy was carried out by Zamarrano et al., who found significant fire retardant effects in epoxy resins [23].

The effect of the nanofillers in polymer composites on the glass transition behavior of the polymer matrix has been studied. In some

---

* Corresponding author. Tel.: +1 414 288 7065; fax: +1 414 288 7066.
E-mail address: charles.wilkie@marquette.edu (C.A. Wilkie).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.06.001

cases, increases in the glass transition temperature (T_g) have been reported [24,25] while in other cases, decreases in T_g are observed [26]. Molecular dynamics simulations of the polymer melts in the presence of nanoparticles have shown that the dynamics of the polymer melts can be influenced by the polymer–nanoparticle interactions [27].

Normally, an attractive polymer–filler interaction should suppress polymer motion, and then, an increase in T_g is expected in nanocomposites with good filler–polymer compatibility [28].

In this investigation, a series of undecenoate-containing LDHs of ZnAl, MgAl, CaAl, NiAl, CoAl and CuAl have been prepared and characterized. The effect of these LDHs on the glass transition, dispersion, thermal and fire properties of their PMMA composites are evaluated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), benzoyl peroxide, zinc nitrate hexahydrate (98%), cobalt(II) nitrate hexahydrate (98%), calcium nitrate tetrahydrate (ACS reagent), magnesium nitrate hexahydrate (99%), copper(II) nitrate hydrate (98%), and aluminum nitrate nonahydrate (98%) were obtained from Aldrich Chemical Co. Nickel(II) nitrate hexahydrate (99%), 10-undecenoic acid (99%), and sodium hydroxide, extra pure pellets, were purchased from Acros Organics. All chemicals were used without further purification. MMA monomer was passed through an inhibitor remover column before use.

2.2. Preparation of LDHs

The preparation and characterization of undecenoate-containing LDHs have been previously described [29]; the co-precipitation method is used and this strategy involves addition of an M^{II}/M^{III} metal salt solution to a basic solution of the desired anions under nitrogen atmosphere to exclude CO_2 which would lead to the formation of carbonate-LDHs [30].

2.3. Preparation of LDHs/PMMA nanocomposites

The PMMA/LDHs nanocomposites were prepared as follow: the appropriate LDH loading was combined with MMA, total weight 140 g, in a 400 ml beaker covered with aluminum foil, and the mixture was stirred vigorously for 1 day. Then, the initiator, 0.1% BPO was added, and the mixture was heated to 70 °C until viscous. The viscous mixture was then heated to 100 °C for 24 h and 120 °C for 3 h to yield the LDH/PMMA nanocomposites. Finally, the polymer was placed overnight in a vacuum oven at 100 °C to remove unreacted monomer. For the two types of LDH composites prepared in this study, the LDH loadings used with PMMA were 3 and 6%.

2.4. Glass transition temperature, T_g and molecular weight measurements

The glass transition temperature (T_g) of the pure polymers and various PMMA/LDH composites were characterized with a differential scanning calorimeter (DSC822 Mettler Toledo using a FRS5 ceramic sensor). All samples were subjected to the following heating/cooling profile: the sample was heated from 50 to 130 °C at 20 °C/min and cooled at 20 °C/min from 130 back to 50 °C. Then, the sample was maintained for 50 s at 50 °C, and then reheated from 50 to 170 °C to obtain the second heat-flow result. From the step change of the reversible heat flow of the second heating, T_g was determined. Temperature in the DSC is reproducible to ± 0.5 °C.

The molecular weight of PMMA and PMMA/LDH composites were obtained from viscosity data. PMMA/6%LDH samples were extracted for 4 days with acetone in a Soxhlet apparatus to dissolve the polymer, leaving behind the LDH, and the polymer was dried in air (12 h) and then in a vacuum oven at 80 °C (12 h). The results are an average of three determinations, and the Mark–Houwink constants were obtained from published data [31].

To investigate the effect of the solvent on the LDH alone, the undecenoate-LDHs were also extracted with acetone for 2 days and the collected powder was dried at room temperature and then in a vacuum oven at 60 °C for 12 h. X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) of the LDH after extraction were obtained and compared with the original samples.

2.5. Characterization of LDH and PMMA/LDH systems

Fourier transform infrared spectroscopy (FT-IR) of the solid materials was obtained on a Bruker Tensor 27 series, with a Pike Miracle ATR accessory using a ZnSe crystal.

TGA was performed on a Netzsch TG 209 F1 instrument at the 15 mg scale under a flowing air atmosphere at a scan rate of 20 °C/min. Temperature is reproducible to ±1 °C and mass to ±0.2%. TGA experiments were done in duplicate and the averages are reported. XRD data was obtained using a Rigaku Miniflex II desktop X-ray diffractometer; data acquisition was performed using a scan speed of 2°/min, at a sampling width of 0.020° from 2 to 40 (2θ) for LDHs and 2 to 10 (2θ) for polymeric samples. Bright field transmission electron microscopy (TEM) used a JEOL 1230 MSC SI033 microscope equipped with a Tietz F224 digital camera, operated at an accelerating voltage of 100 kV. Cone calorimeter measurements were performed on an Atlas CONE-2 according to ASTM E 1354 at an incident flux of 50 kW/m^2, using a cone shaped heater; the exhaust flow was set at 24 L/s. The specimens for cone calorimetry were prepared by the compression molding of the sample (about 30 g) into 3 mm × 100 mm × 100 mm square plaques. Typical results from cone calorimetry are reproducible to within about ±10%; these uncertainties are based on many runs in which thousands of samples have been combusted [32].

3. Results and discussion

3.1. Characterization of the M^{II}/Al/undecenoate LDH series

3.1.1. XRD characterization of the M^{II}/Al/undecenoate LDH series

XRD traces of the M^{II}/Al/undecenoate LDH series where the divalent metal cations were varied are shown in Fig. 1. All the diffraction peaks are in good agreement with layered structures; the diffrac-

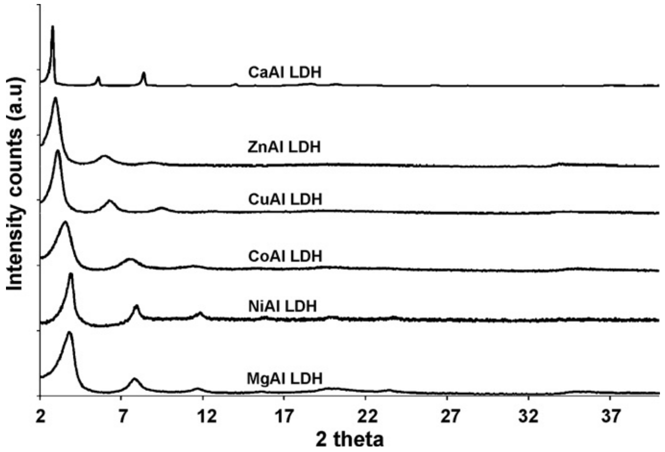

Fig. 1. XRD patterns of the undecenoate-containing LDHs of MgAl, NiAl, CoAl, CuAl and ZnAl.