



Isothermal crystallization and melting behavior of polypropylene/layered double hydroxide nanocomposites

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ABSTRACT

The effect of layered double hydroxide (LDH) nanolayers on the crystallization behavior of polypropylene (PP) was studied based on the preparation of nanocomposites by a melt intercalation method. The isothermal crystallization kinetics and subsequent melting behavior of PP/LDH hybrids were studied with differential scanning calorimetry (DSC), polarized optical microscopy (POM), and wide-angle X-ray diffraction (WAXD). Studies revealed that the LDH promoted heterogeneous nucleation, accelerating the crystallization of PP. The Avrami equation successfully describes the isothermal crystallization kinetics of PP/LDH hybrids and signifies heterogeneous nucleation in crystal growth of PP. The varying values of Avrami exponent (n) and half crystallization time ($t_{1/2}$) of PP and PP/LDH hybrids describes overall crystallization behavior. The crystallite size (D_{hkl}) and distribution of different crystallites in PP varied in presence of LDH. A significant increase in melting temperature is observed for PP/LDH hybrids. The POM showed that smaller and less perfect crystals were formed in nanocomposites because of molecular interaction between PP chains and LDH. The value of fold surface free energy (σ_e) of PP chains decreased with increasing LDH content. Finally, the overall results signify that LDH at nanometer level acted as nucleating agent and accelerate the overall crystallization process of PP.

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1. Introduction

In recent years, polymer/layered crystal nanocomposites have been recognized as one of the most promising research field in material chemistry. The scientific and technological interest for tailoring and modifying the polymer properties has been driving a very vivid research on the nanostructured materials. In this regard, most emphasis has been given to polymer layered silicate nanocomposites, which after intercalation and exfoliation within the polymer structure, induces substantial increase in the material properties [1–3]. Recently, a new promising class of inorganic layered materials, layered double hydroxide (LDH) has been developed. The LDHs are the class of anionic or hydrotalcite like clays represented by the general formula $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+} \cdot [(\text{A}^{n-})^{x/n} \cdot m\text{H}_2\text{O}]$ where M^{II} and M^{III} are divalent and trivalent metal cations, respectively, and A^- is the interlayer anion (Fig. 1) [4,5]. The typical metal hydroxide-like chemistry and conventional clay-like layered crystalline structure makes LDH potential flame retardant [6] and suitable for polymer nanocomposite preparation. In recent years, polymer/LDH nanocomposites have attracted a great interest because they exhibit improved physical and performance prop-

erties in comparison to the pristine polymers and conventional composites [7–11].

Polypropylene (PP) is one of the most widely used polyolefins and has stimulated intensive research in order to produce polypropylene nanocomposites with enhanced properties. Hence, it is important to investigate method of preparation, structure and properties of PP reinforced with LDH from commercial point of view. It is well understood that physical and mechanical properties of crystalline polymer like polypropylene depend on the morphology, crystalline structure and degree of crystallization. Therefore, the study of the kinetics of crystallization is necessary for optimizing industrial process, conditions and establishing the structure–property correlations in the case of PP/LDH nanocomposites. It was also recognized that some inorganic fillers, as reinforcing agents in composites, can induce nucleation for crystallization and overall crystallization process [12–14]. The isothermal and non-isothermal crystallization kinetics of PP and its composites with different fillers have been extensively reported in the literature [12–18]. It has been found that the degree of crystallinity, crystal size, and shape morphology and crystallization kinetics of the polypropylene matrix is strongly affected by the presence of nano-scale particulates. Recently, Chen et al. [13] calorimetrically studied the isothermal crystallization behavior of PP/polyhedral oligomeric silsesquioxane (POSS) nanocomposites and found that POSS nanoparticles could accelerate the overall crystallization of

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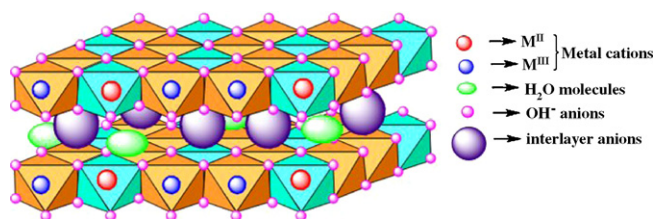


Fig. 1. Layered crystal structure of hydrotalcite-like compounds.

PP and suggested a three-dimensional growth with heterogeneous nucleation. Maiti et al. [18] investigated how crystallization controls of the fine structure and morphology of the PP/clay nanocomposites. They concluded that the clay platelets act as a nucleating agent and lower the size of the PP spherulites.

To our knowledge, only few articles report the use of such inorganic/organic (I/O) LDH/surfactant assemblies as filler for polymers and their effect on the iso or non-isothermal crystallization behavior and the subsequent effect on changes of the microstructural parameters [19–21]. However, there was no literature on studies of LDH induced isothermal crystallization and melting behavior of polypropylene. The purpose of this article was to investigate the influence of LDH type nanometric anionic clays, organo-modified by surfactant molecules as filler on the isothermal crystallization behavior of PP in PP/LDH hybrid nanocomposites. Melting behaviors following the isothermal crystallization process were also discussed. The layered structure and the dispersed morphology of LDH in PP matrix were confirmed by X-ray scattering (WAXD) and transmission electron microscopy (TEM), respectively. The data obtained from differential scanning calorimetry were employed for measuring crystallization kinetic parameters and subsequent melting. The crystallization kinetic parameters and thermal characteristics based on isothermal crystallization of the PP and PP/LDH composites were achieved by confronting Avrami equation. The spherulitic growth rate was used to obtain data on the specific surface free energies for the PP and all nanocomposites. The microcrystalline dimensions (D_{hkl}) of crystal growth and spherulitic morphology were investigated by WAXD and optical polarising microscopy (POM), respectively.

2. Experimental

2.1. Materials

The isotactic polypropylene used in this study is Exxon Mobile PP with 2.5–3.5 MFI. The maleic anhydride-grafted PP polymer (PP-g-MA) used as compatibilizer was a low molecular weight Polybond 3200 (MA content 1%, density 0.91 g/cm³ and Mw 90,000) obtained from Chemtura corporation. Dodecyl sulfate modified LDH, i.e. Mg₂Al-DS LDH was prepared obtained through courtesy of Dr. Fabrice Leroux, University of Blaise Pascal, France.

2.2. Nanocomposite preparation

Nanocomposites containing 1%, 3% and 5% LDH nanoparticles were prepared by melt mixing in two steps using a co-rotating tightly intermeshed twin-screw extruder (DSM microcompounder). All materials were dried at 80 °C under vacuum prior to mixing.

2.2.1. Step 1: preparation of compatibilized PP

Isotactic polypropylene was mixed with MA-g-PP in a weight proportion of 95:5. The operation temperature was maintained at 180 °C for 5 min at 200 rpm rotor speed to prepare a master batch of

compatibilizer in PP. All experiments were performed under inert atmosphere.

2.2.2. Step 2: preparation of composites

The designated amount of Mg₂Al-DS LDH was added to the molten compatibilized PP and mixed at 180 °C for 5 min keeping other parameters as above. The samples were abbreviated as PPL1, PPL3 and PPL5 for 1%, 3% and 5% loading in PP, respectively.

The films of thickness between 80 and 100 μm were obtained using laboratory press at 180 °C under 4 tonnes of pressure for 2 min.

2.3. Microstructure characterization

The degree of LDH nanolayer dispersion was analysed by WAXD with Rigaku (Japan) D/max-RB wide-angle X-ray diffractometer (WAXD). The operation parameters were Cu K α radiation at a rotating anode generator operated at voltage of 40kV and at current of 100 mA. The scanning rate was 2°/min at an interval of 0.02°. Samples for TEM imaging were sectioned using a Leica Ultracut UCT microtome at 80–100 nm thickness with a diamond knife at –100 °C. The sections were collected from water on 300 mesh carbon-coated copper grids. TEM imaging was done using a JEOL 1200EX electron microscope operating at an accelerating voltage of 100 kV. Images were captured using a charged couple detector camera and viewed using Gatan Digital Micrograph software.

2.4. Crystallization behavior

The isothermal crystallization kinetic measurements were carried out with a TA instruments Q10 differential scanning calorimeter (DSC) calibrated with indium. The samples of PP and PP/LDH nanocomposite about 200 μm thick were obtained by hot compression molding, disk-like samples about 5 mg weight were taken for DSC measurements. Samples were heated to 200 °C at a rate of 10 °C/min under a nitrogen atmosphere and held for 5 min to destroy any residual nuclei. Then it was rapidly cooled to certain isothermal crystallization temperatures (T_c), and held to allow complete crystallization. After the isothermal crystallization was finished, the samples were heated to 200 °C at a rate of 10 °C/min to estimate melting profile of the samples.

To support the isothermal crystallization events and kinetic results analyzed by DSC thermograms, a very thin section of samples were observed under crossed polarizers with a polarizing LEICA-DMRX optical microscopy (POM). A thin sample sandwiched between two glass cover slips was placed inside the Linkam shearing device (CSS450) and the temperature was raised to 200 °C at the rate of 30 °C/min, kept at that temperature for 5 min, and then rapidly cooled to 128 °C for isothermal crystallization for 20 min. The morphological features (optical texture images) were captured in Olympus CCD camera.

3. Result and discussion

3.1. Nanocomposite microstructure

The crystallization behavior of nanocomposites is strongly influenced by the dispersion state of nanolayers in polymer matrix, which can be analyzed from X-ray diffractions [22]. The complete disappearance of WAXD peaks may reveal high degree of exfoliation or the presence of small diffracting volume as in the cases of low filler loading. It must be taken into account that disappearance of diffraction peaks are not sufficient argument to recognize exfoliated structures. Direct observation by TEM is then necessary to characterize an exfoliation state. Fig. 2(a–d) shows WAXD analysis

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