

Fire retardancy of polymer clay nanocomposites: Is there an influence of the nanomorphology?

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ABSTRACT

The obvious aspect of nanodispersion and its role when investigating fire retardancy is not often clearly commented upon in the literature. Polymer clay nanocomposites can exhibit different morphologies and these might have consequences for their fire behaviour. Using solid state NMR to quantify the nanodispersion of organoclay in polyamide-6 (PA-6), we have prepared by melt blending PA-6/clay nanocomposite exhibiting different nanomorphologies. NMR results are consistent with transmission electron microscopy (TEM) images but the advantage of NMR is that it is representative of the whole sample and provides a precise quantification. PA-6 nanocomposites exhibit significant reduction of PHRR but the nanomorphology (exfoliation, intercalation and presence of tactoids) does not play any significant role. In other words, we have clearly shown that if nanodispersion is achieved, polymer/clay nanocomposite should exhibit fire retardant properties.

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1. Introduction

Polymeric materials are commonly used in everyday life, increasing fire hazards, and so fire retardants are often incorporated into them to limit their flammability [1]. This approach is often preferred to using low flammability polymeric materials because it is a better compromise between cost and properties. Nevertheless, the total loading usually lies between 15 and 25 wt.% to achieve acceptable performance. In some cases, they modify the other properties of the polymer like the mechanical properties. Moreover the processing has to be done within an appropriate and limited window (temperature, shear, etc.).

Of particular interest is the developed nanocomposite technology consisting of a polymer and organically modified montmorillonite (MMT) because they often exhibit remarkably improved mechanical and various other properties compared to those of the virgin polymer [2]. It was reported that polyamide-6 (PA-6) nanocomposites exhibit improved properties including a high storage modulus both in the solid and melt states, increased flexural properties, a decrease in gas permeability, and increased heat distortion temperature. Gilman et al. reported that the presence of nanodispersed montmorillonite (MMT) clay in polymeric matrices produces a substantial improvement in fire performance at loadings as low as 3–5 wt.% [3–5]. The nanocomposites exhibit

low flammability in terms of heat release rate (HRR). Depending on the polymer, the peak HRR can be decreased by between 50% and 70% in a cone calorimeter experiment. For example, the peak HRR of polyamide-6 (PA-6)/clay nanocomposites is decreased by 63% compared to virgin PA-6 at an external heat flux of 35 kW/m².

The obvious question of nanodispersion when investigating fire retardancy is not always addressed in the literature, and it is often assumed when incorporating the so-called nanoparticles that a polymer nanocomposite is formed. The first question is then: what is the role of the nanodispersion? To answer this question, we may take as a representative example a poly(ethylene-co-vinyl acetate) (EVA) containing MMT clay. MMT clays organomodified by methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (C30B) and raw MMT (Na⁺) was melt blended with EVA (EVA containing 19% vinyl acetate) according to a protocol described in Ref. [6]. EVA-C30B exhibits an intermediate structure between exfoliated and intercalated, determined both by X-ray diffraction and by transmission electron microscopy (TEM), while EVA-Na⁺ is a microcomposite. Cone calorimetry experiments reveal that the peak heat release rate (HRR) is decreased by 25% for the microcomposite (EVA-Na⁺) and by 50% for the nanocomposite (EVA-C30B) compared to the virgin EVA (Fig. 1). This result suggests (qualitatively speaking) that real nanodispersion should be achieved to get the lowest flammability. Similar conclusions were also reported in other published works [7,8]. Zheng and Wilkie [9] extend those conclusions in a more general way suggesting, based on his works and on literature that no reduction or a slight

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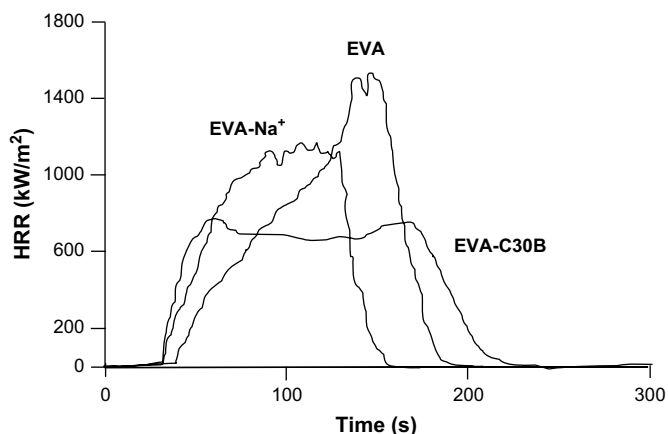


Fig. 1. Comparison of the heat release rate (HRR) plots for pure EVA, EVA-Na⁺ (microcomposite) and EVA-C30B (nanocomposite) at 50 kW/m² heat flux with a mass fraction of 5% layered silicate (from Ref. [6]).

reduction in HRR peak can be taken as an indication that nanocomposite formation has not occurred. A quick overview of the literature indicates that this is probably true [6–9].

Polymer clay nanocomposites can exhibit different morphology but from the discussion above no assumption may be made about its role in the fire behaviour. It is our goal in this paper to try to answer this question. In general, polymer clay composites fall into three categories [10]: (i) microcomposites: the clay tactoids exist with no penetration of the polymer into the clay lamellae; (ii) exfoliated composites: the individual clay layers are dispersed as single platelets into a continuous polymer matrix; (iii) intercalated composites: in an intercalated composite the insertion of polymer into the clay structure occurs so as to swell the spacing between platelets in a regular fashion, regardless of the clay to polymer ratio. The characterization of the morphology is traditionally done using transmission electron microscopy (TEM) and X-ray diffraction (XRD) [12]. TEM provides essential information on the structure of the nanocomposite. It gives qualitative information and extensive imaging is required to insure a representative view of the whole material. Other methods, such as small angle X-ray scattering (SAXS) [13], and rheological measurements [14], also serve to complement the XRD and TEM data. The main drawbacks of these techniques are that they cannot quantify the degree of nanodispersion in the bulk polymer. A quantitative approach has been developed at NIST using solid state nuclear magnetic resonance (NMR) [15–17]. The method is based on T_1^H (proton longitudinal relaxation time) measurement. It utilizes two effects: (1) the paramagnetic character of this MMT which directly reduces the spin-lattice relaxation time (T_1^H) of nearby protons and (2) spin diffusion, whereby this locally enhanced relaxation propagates to more distant protons. The interpretation of those effects allows two parameters to be extracted relating to the dispersion. The first parameter, f , is the fraction of the potentially available clay surface which has been transformed into polymer/clay interfaces. The second parameter, ϵ , is a relative measure of the homogeneity of the dispersion of these actual polymer/clay interfaces. These parameters will be discussed in the following parts of this paper to characterize the morphology of polymer clay nanocomposite and to quantify the degree of nanomixing.

The ultimate goal of this work was to examine the effects of the nanomorphology on the fire behaviour of polymer clay nanocomposite using PA-6 as typical example. Different PA-6 clay (nano)composites (from microcomposite to well exfoliated nanocomposite) were prepared, and the quantitative characterization of the structure is presented and discussed in the first part of the

paper. In the second part, well characterized and comparable nanocomposites were evaluated by cone calorimetry and the reaction to fire of those materials as a function of the nanomorphology is discussed.

2. Experimental

2.1. Materials and preparation of the nanocomposites

PA-6 was supplied by Rhodia (France) under the trade name Technyl S27. Montmorillonite (MMT) clay originated from Southern Clay Products, Inc. (Gonzales, TX, USA). The starting material, sodium-MMT (Cloisite Na⁺, hereafter called CNa⁺), was commercially modified using methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (Cloisite 30B, hereafter called C30B) or using dimethyl, dihydrogenatedtallow, quaternary ammonium (Cloisite 20A, hereafter called C20A). MMT was dried overnight at 110 °C before use.

PA-6 was melt-mixed with the clay using a Brabender mixer running under nitrogen at 50 rpm and at 250 °C. The clay loading (Cloisite Na⁺, Cloisite 20A and Cloisite 30B) was 5 wt.% organoclay. The true silicate concentration used in our calculation was determined by heating the dry, post-extrusion pellets in a tubular furnace to 800 °C for 12 h, and correcting for structural rearrangement by dividing the ash percentage by 0.935 (the silicate rearrangement results in 6.5% loss of structural water).

2.2. NMR spectroscopy

The direct influence of the paramagnetic Fe³⁺, embedded in the aluminosilicate layers of the MMT, on polymer protons within about 1 nm from clay surfaces creates “relaxation sources” which, via spin diffusion, significantly shorten the overall T_1^H . We used T_1^H as an indicator of the nanodispersion of the clay and spin diffusion modelling was used to describe this phenomenon and to quantify the degree of nanodispersion. The main expectation is that, for a given overall clay concentration, the better the dispersion of single MMT layers, the shorter is the average T_1^H . T_1^H measurements can therefore be used to probe the dispersion at the nanoscale of MMT in the polymer. This approach was fully described in one of our papers [16] and here, we will quickly remind the reader of the principles of the method.

Our approach is to simulate a spin-lattice relaxation experiment considering a very well exfoliated system (perfectly stratified system). The model consists of two distinct domains: the region of the paramagnetic source and the region of the polymer (PA-6). To simplify the calculation, the assumptions are as follows: (a) the intrinsic T_1^H for the polymer layers in the nanocomposite is the spin diffusion averaged T_1^H of the pure polymer, (b) MMT platelets are parallel to one another and equally spaced (Δ is the platelet-platelet spacing), and (c) the paramagnetic influence of the Fe in the clay is replaced and mimicked by a fast-relaxing thin layer of PA-6 (we assume 0.4 nm as was done in the case of PS nanocomposite) whose protons are in spin diffusion contact with the rest of the polymer. By modelling the problem as we have done, all we are creating is a relaxation source whose somewhat arbitrary width is tightly coupled to the relaxation time. Before starting any computation, we need to estimate Δ , the platelet-platelet spacing. Our model assumes a regular, repeating lamellar structure of alternating clay and PA-6; then the spacing can be calculated by $\Delta = (V_{\text{clay}}/V_{\text{tot}}d_{\text{clay}})^{-1}$ where V_{clay} and V_{tot} are, respectively, the fractional volume occupied by the clay and the total volume in the nanocomposite. Hence, using a thickness, d_{clay} , of 1.0 nm for each clay layer, the densities of $\rho_{\text{PA-6}} = 1.13 \text{ g/cm}^3$ for PA-6 and $\rho_{\text{clay}} = 2.86 \text{ g/cm}^3$ for MMT, and mass fractions determined from

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