



Probing the confining effect of clay particles on an amorphous intercalated dendritic polyester



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ABSTRACT

The fourth generation of a hydroxylated dendritic hyperbranched polyester (HBP) was combined with sodium montmorillonite clay (Na⁺MMT) using water to generate a broad range of polymer clay nanocomposites from 0 to 100% wt/wt Na⁺MMT. Analysis with differential scanning calorimetry (DSC) showed a deviation in heat capacity, ΔC_p , with clay content at the T_g from a two-phase trend which was attributed to the formation of an immobilized rigid amorphous fraction (RAF) in the interlayer spacing of the intercalated system. This deviation occurred in a step-like fashion which we attributed to 0.5 nm incremental changes in the interlayer spacing, previously observed through X-ray diffraction analysis. A simple series model was utilized to quantify these interlayer spacings based on the ΔC_p values and showed good correspondence with the X-ray results. The RAF was quantified from changes in heat capacity with clay content and was verified by an alternative novel positron annihilation lifetime spectroscopy (PALS) approach. The PALS quantification of the RAF was possible through an analysis of changes in the hole size thermal expansivity of the nanocomposites as a function of clay composition. Results indicated that as much as 32% by weight of the system is made up of the RAF at its maximum.

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1. Introduction

Polymer clay nanocomposites often exhibit chemical and physical properties that are superior to those of conventional composite materials [1–3]. The morphology of these nanocomposites can generally be classified as phase separated, intercalated, disordered intercalated, or exfoliated, depending on the interactions between the nanoclay and the polymer as well as the processing conditions [1–3]. To promote dispersion in a polymer matrix, layered silicates such as sodium montmorillonite (Na⁺MMT) typically require modification by surfactants to increase the organophilicity of the clay surfaces.

Various water-soluble linear polymers, such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), and poly(vinylpyrrolidone) (PVP), have successfully been intercalated into unmodified Na⁺MMT clay galleries by aqueous solution casting methodologies [1,2]. However, the high viscosities of these systems can require shear intensive processing procedures, especially at

high clay contents [4]. Hyperbranched polymers (HBPs) possess lower solution viscosities than linear polymers due to their more compact globular structures [5], which facilitate solution processing, even at high clay concentrations, without shear intensive procedures.

Due to their facile synthesis [6–9], dendritic hyperbranched polyester polyols (also known as Boltorn™ dendritic polyols) based on 2,2-bis-methylpropionic acid (bis-MPA) with an ethoxylated pentaerythritol core are popular model systems which preserve the essential features of dendrimers, namely high end-group functionality and a globular architecture, but possess imperfect branching and large polydispersities [5–16]. These HBPs are hydrophilic due to the presence of branch-terminal hydroxylated end groups [17], and hence are compatible with clay gallery surfaces. Experimental [18–22] and theoretical [23] studies indicate that a high interaction strength between the end functional groups of the dendritic polymers and a substrate leads to the collapse and flattening of the globular dendritic structure on the substrate.

The incorporation of polymer into clay galleries exposes numerous interfaces to the polymer matrix and the resulting polymer-substrate interactions can be probed by bulk techniques. Manson et al. [24–27] explored the structure of intercalated

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nanocomposite films based on surfactant-free Na⁺MMT clays mixed with second, third, and fourth pseudogeneration BoltornTM dendritic polyols. X-ray diffraction (XRD) data demonstrated that, at intermediate Na⁺MMT contents, the interlayer spacings of the intercalated nanocomposites correlated closely with estimates of the molecular diameters of the different HBP generations. It was concluded that the HBPs maintained their globular architecture in an intercalated state throughout approximately half of the compositional range. However, at the higher clay contents, the HBPs flattened within the clay galleries, leading to equivalent interlayer spacings for the 2nd, 3rd, and 4th HBP generations.

Subsequently, we carried out a more detailed morphological analysis of the same intercalated nanocomposite system [28], specifically comprising of the 2nd and 4th pseudogenerations of Boltorn dendritic polyols and encompassing polymer clay nanocomposite compositions from 0 to 95% wt/wt Na⁺MMT. Intercalation peaks were observed by powder XRD at and above 15% wt/wt Na⁺MMT content for both HBP systems. In fact, intercalation was present at all clay loadings, as evidenced by TEM, but, at lower clay contents, exfoliated and disordered intercalated states were also present. The number of clay layers per intercalated stack increased with increases in Na⁺MMT content. The interlayer spacings for the 2nd and 4th pseudogenerations (HBP2 and HBP4) were observed to decrease in increments of approximately 0.5 nm as the clay content increased. Importantly, the interlayer spacings for the 2nd and 4th generations of HBP were nearly identical at the same clay compositions, indicative that the interlayer spacings were independent of the HBP generation number. The interlayer spacings for both HBP2 and HBP4 decreased with increasing clay content until finally reaching a minimum spacing of 0.5 nm at the highest clay contents. These step-wise changes in interlayer spacings are consistent with the presence of discrete layers of flattened HBP between the clay layers. It was proposed that the HBP adsorbed onto the clay layers in solution and re-aggregated, upon solvent removal, into intercalated stacks of clay and flattened HBP. Recently, layer-by-layer intercalation of flattened BoltornTM HBPs into Na⁺MMT clay galleries was confirmed by Androulaki et al. [29]. Analogous behavior was observed for Na⁺MMT clay based nanocomposites with a hyperbranched polyesteramide (HybraneTM) and a polyamidoamine (PAMAM) dendrimer, each prepared via aqueous solution intercalation methodology [30,31]. Therefore, this trend appears to be fairly general for hydrophilic dendritic systems.

The confinement of collapsed HBP between multiple clay layers is expected to result in a sizable amount of immobilized polymer. The nature of this immobilized polymer is viewed as analogous to the concept of a rigid amorphous fraction (RAF) in semi-crystalline polymers, introduced to explain an observed discrepancy between the degree of crystallinity and the change in heat capacity, ΔC_p , at the glass transition, T_g [32]. In simplest terms, RAF represents the fraction of the amorphous phase that does not contribute to the change in ΔC_p at either the T_g or T_m (melting). It is well-established [32–44] that the RAF is due to an immobilization of the disordered polymer chains that connect the crystalline lamellae. These chains are unable to undergo long range translational motions when crystalline constraints are imposed during crystallization of the polymer melt, implying that the RAF vitrifies in the vicinity of the crystallization temperature, T_c . In contrast, the un-constrained amorphous chains, the mobile amorphous fraction (MAF), remain in the molten state at T_c and vitrify upon cooling at the regular T_g . Complete devitrification of RAF occurs at T_m .

It is also established that the immobilized amorphous phase in nanocomposites exhibits some of the characteristics of a RAF, such as the suppression of the glass transition [45–48]. The majority of recent research on RAF at the particle interface has involved SiO₂ nanocomposites that utilize ΔC_p analysis at the T_g to measure the

amount of RAF [49–54] and has focused on semicrystalline polymer nanocomposite systems [55–61].

Unlike crystalline phases, however, inorganic clay does not melt within the thermal stability range of the polymers. This means that, if the interactions between polymer and inorganic substrate are maintained at elevated temperatures, devitrification of the immobilized chains does not occur [45]. Indeed, this was demonstrated in a study of the dynamics of an amorphous hyperbranched polyesteramide intercalated in Na⁺MMT layers via quasi elastic-neutron scattering [62]. It was observed that the polymer chains confined within the clay galleries exhibit dynamical behavior above the bulk T_g similar to that of the bulk polymer below the T_g . The HBP dynamics were frozen due to the clay nanoconfinement, consistent with observed decreases in ΔC_p at the T_g [62].

In the current paper we study the behavior of the immobilized RAF in surfactant-free Na⁺MMT clay nanocomposites generated using the 4th generation of a BoltornTM dendritic polyol over a very broad range of compositions (0–100% wt/wt). Since the Na⁺MMT exhibits no thermal transitions within the investigated temperature ranges, it is ideally suited to investigate polymer immobilization solely at the clay interfaces. Heat capacity measurements were used to quantify the amount of RAF as described by Wunderlich et al. for semicrystalline polymers [32]. We demonstrate that the heat capacity behavior shows a strong correlation with the earlier observed step-like behavior of interlayer spacing in these intercalated nanocomposites [28,29]. To probe the structure of the RAF, free volume measurements using positron annihilation life-time spectroscopy (PALS) were employed.

PALS is a well-established, quantitative probe for free volume in polymeric materials [63,64]. In a PALS experiment, high energy positrons are injected from a radiation source into a polymer sample. The positrons thermalize via collisions with atoms and either annihilate or form a hydrogen-like pair with a secondary electron created via collision-induced ionization. In polymers, the more stable pair system, called an ortho-positronium (o-Ps), tends to localize in regions of low density, i.e. holes. Annihilation of such localized o-Ps occurs via a pickoff mechanism in which the o-Ps positron annihilates with an electron of the medium with an opposite spin. Quantitative comparisons have been established between the characteristic parameters, obtained via PALS, viz. the intensity, I_3 , and lifetime, τ_3 , of the o-Ps annihilation component, and the fractional free volume, f_v , of amorphous polymers, as computed by statistical mechanical theory [65,66]. The o-Ps intensity, I_3 , is typically regarded as a measure of the number density of the free volume holes. The o-Ps lifetime, τ_3 , can be related to a spherical hole radius, R , via the Tao-Eldrup equation, which is based on quantum mechanical and empirical arguments [67,68] as follows:

$$\tau_3 = 0.5 \text{ (ns)} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} \quad (1)$$

where R is the hole radius in Å. R_0 equals $R + \Delta R$ where ΔR is a fitted empirical electron layer thickness of 1.66 Å. From R , the average hole free volume $v_h = (4\pi/3)R^3$ may be calculated. It follows that f_v is proportional to the product $I_3 v_h$.

As mineral silicate layers are too dense for o-Ps species to form, PALS is only sensitive to the HBP content of the HBP/clay nanocomposites. PALS experiments were used to assess, as a function of clay content, the average free volume hole size below and above the glass transition of the nanocomposites. The broad range of compositions prepared in this study enabled a novel opportunity to examine the free-volume behavior in intercalated polymer/clay nanocomposites. We anticipated that the RAF, which remains in the

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