Hyperbranched Polymer Layered Silicate Nanocomposites

Christopher J. G. Plummer,[†] László Garamszegi, Yves Leterrier, Marlene Rodlert, and Jan-Anders E. Månson*

Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The development of polymer nanocomposites incorporating intercalated or exfoliated layered silicate clays such as sodium montmorillonite (Na+MMT),[1] has been substantially driven by the discovery of large increases in strength and stiffness in polyamide containing less than 5 wt % exfoliated clay.[2−4] The concept has since been extended to other systems, including epoxides and polyurethanes,[5−8] with emphasis on identifying conditions and/or formulations that promote exfoliation.[9−11] Dispersion of the silicate layers in the polymer or precursor often requires replacement of the exchange cations of the native clay by organophilic cations to compatibilize the interlayer galleries with other organic species. Certain polymers nevertheless show strong intrinsic interactions with native clays, owing for example to solvation of the interlayer cations by polar groups, and water-assisted preparation of exfoliated poly(vinyl alcohol) (PVOH)/Na+MMT nanocomposites has been demonstrated.[12,13] However, in many cases, bridging effects lead to re-aggregation on drying, as reported for dispersions of Na+MMT in aqueous poly-(ethylene oxide)[13] and poly(vinyl pyrrolidone).[14]

An alternative is to use a dendrimer with a high density of hydrophilic end groups and an interior with less affinity for the clay. Collapse of the dendrimer onto the substrate will be limited sterically and because of its amphiphilic character, and it may hence be possible to achieve intercalation with larger gallery spacings than for linear polymers with equivalent functional group densities, facilitating exfoliation. To explore this idea, we have mixed Na+MMT (cation-exchange capacity: 92 mequiv/100 g) with aqueous dispersions of −OH
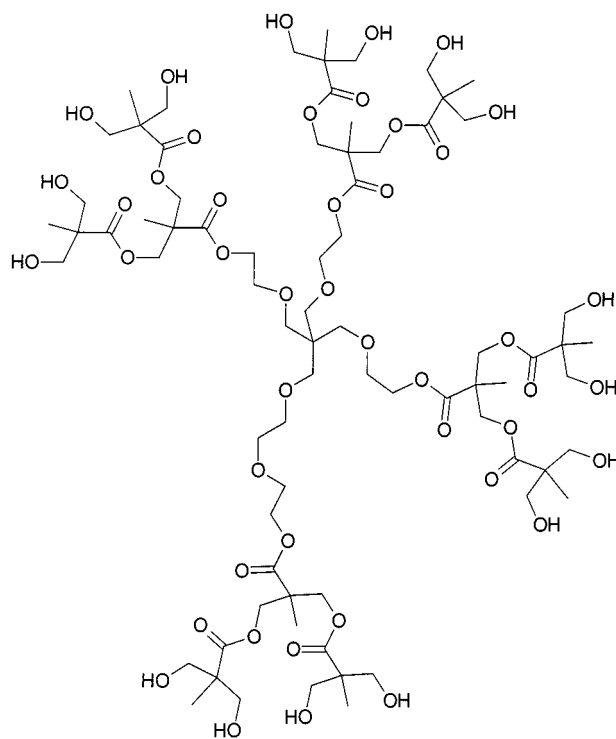
* To whom correspondence should be addressed. Tel.: 0041 (0)21 693 4281. Fax: 0041(0)21 693 5880. E-mail: jan-anders.manson@ epfl.ch.
† E-mail: christopher.plummer@epfl.ch.

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Figure 1. Chemical structure of the dendrimer analogue of the second pseudo-generation HBP.

Table 1. Materials Parameters for the HBPs

pseudo-generation	M_n (g/mol)	−OH/molecule	T_g (K)
2	1740	16	298
3	3588	32	309
4	7284	64	313

terminated hyperbranched polyesters (HBP, Perstorp), prepared by condensation of 2,2-bis-hydroxymethyl propionic acid (bis-MPA)[15] with a tetrafunctional ethoxylated pentaerythritol core, giving structures analogous to the dendrimer shown in Figure 1.

Although characterized by imperfect branching and significant polydispersity,[16] HBPs conserve the essential features of dendrimers, namely, high end-group functionality and a globular architecture.[17] Moreover, they are inexpensive to produce and hence of great interest as reactive components in thermoset or UV curable coatings, where exfoliated silicates could have benefits for barrier properties, for example.[18,19] The number-average molar mass, M_n, and −OH functionality (Table 1) were derived assuming all the bis-MPA monomers were to react with a core molecule, so that M_n is the total molar mass divided by the number of cores. However, cyclization of the bis-MPA may occur, and the values in Table 1 should only be considered indicative. Each grade is defined by a pseudo-generation number,

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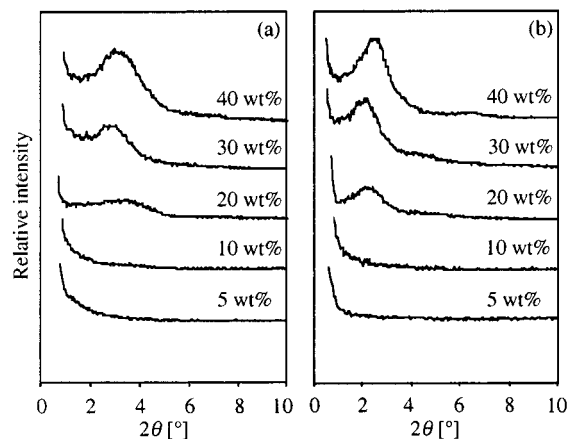
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Figure 2. WAXS patterns for HBP/Na⁺MMT blends with different compositions: (a) second pseudo-generation HBP; (b) fourth pseudo-generation HBP.

such that the *N*th pseudo-generation corresponds to a reaction mixture containing $4\{1 + 2 + 2^2 + ... + 2^{N-1}\}$ bis-MPA molecules per core, as for an *N*th generation dendrimer. Size exclusion chromatography (SEC) and viscosity measurements in different solvents indicate a weak dependence of the intrinsic viscosity on molar mass and hence dendrimer-like configurations.[20]

HBP−clay composites were prepared by introducing the required amount of Na⁺MMT to 10 g of HBP dispersed in 75 mL of boiling deionized water. The mixture was stirred in air at 50 °C with a magnetic stir bar. After evaporation of half the water, the resulting gel was transferred to an open silicone rubber mold and dried in air for 2 days at 50 °C. The remaining solid was dried for another 2 days at 120 °C under vacuum, ground, and pressed into 25-mm-diameter 1-mm-thick disks at 60 °C for wide-angle X-ray scattering (WAXS, Siemens Kristalloflex 805). At high Na⁺MMT contents, WAXS indicated 2.5−2.8, 2.8−3, and 3.6−3.9 nm silicate layer basal spacings for the second, third, and fourth pseudo-generation HBPs, respectively, as opposed to 1.06 nm for the as-received Na⁺MMT. The corresponding WAXS peaks disappeared as the clay content was reduced below 20 wt % for all the HBPs (Figure 2), consistent with previous observations of PVOH/Na⁺-MMT nanocomposites prepared under similar conditions.[12] In this range of compositions, the specimens were transparent and individual clay particles were no longer visible by optical microscopy. TEM (Philips EM340) of microtomed thin sections from specimens containing 20 wt % Na⁺MMT revealed stacks of 5−10 silicate layers with a relatively well-defined spacing, interspersed with exfoliated silicate layers (Figure 3a). At 10 wt % clay, however, exfoliation was confirmed to dominate (Figure 3b). Similar results were obtained for all the grades. The observation of increasing basal spacings with pseudo-generation number at high clay contents may have reflected the increase in nominal M_n, the interlayer distances' being consistent with estimates of the molecular sizes from self-avoiding rotational isomeric state simulations of the second-, third-, and fourth-generation dendrimer analogues and estimates of the HBP hydrodynamic radii from SEC.[20]
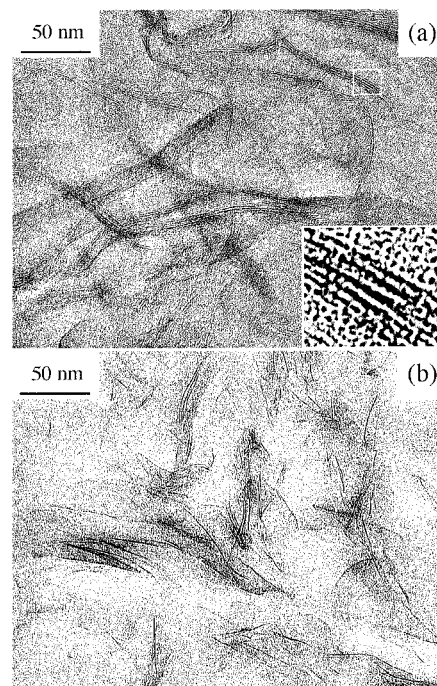
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Figure 3. TEM micrographs of 70-nm-thick sections of second pseudo-generation HBP/Na⁺MMT: (a) 2 wt % Na⁺MMT; (b) 10 wt % Na⁺MMT. The inset in (a) is an enlargement of the region indicated.
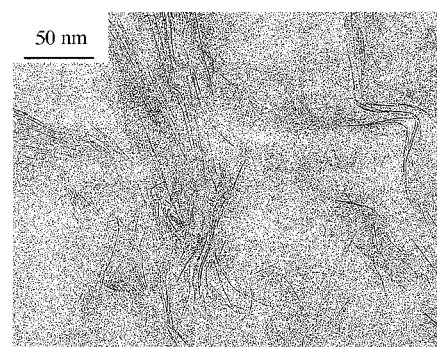

Figure 4. TEM micrograph of a second pseudo-generation HBP/10 wt % Na⁺MMT nanocomposite mixed with a stoichiometric amount of MDI in THF and cured at 120 °C, showing mainly an exfoliated structure.

Practical interest in HBP/Na⁺MMT composites will depend greatly on whether it is possible to redisperse them in an organic solvent and react or modify the functional groups without re-aggregation of the silicate layers. Here, we consider the reaction of the HBP with methyl diphenyl diisocyanate (MDI, Aldrich) to produce a polyurethane network: 30 wt % of a stoichiometric mixture of HBP/Na⁺MMT and MDI was dispersed in dry tetrahydrofuran (THF) under N₂ and stirred for 1 h at 50 °C. The mixture was poured into a dry open silicone mold and the THF evaporated at room temperature under dry N₂ for 1 h, followed by curing at 120 °C under vacuum for 12 h to give 5×1 mm² rectangular cross-section tensile specimens. FTIR showed conversion of the isocyanate groups to be complete. The microstructure of a specimen made from second pseudo-generation HBP/10 wt % Na⁺MMT (4.9 wt % clay overall) is shown in Figure 4, indicating the initial exfoliated state of the silicate layers to be maintained.
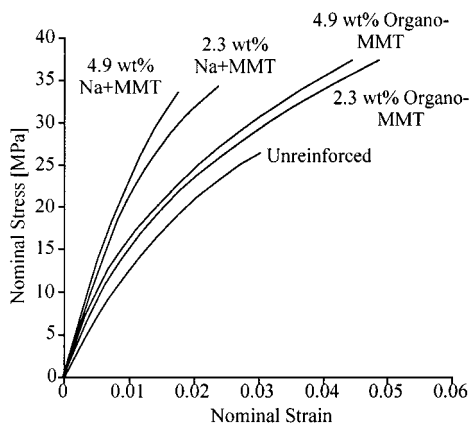
Figure 5. Nominal stress–nominal strain curves for exfoliated second pseudo-generation HBP/Na⁺MMT-based polyurethane nanocomposites and intercalated second pseudo-generation HBP/organically modified MMT composites for the overall compositions indicated (27 °C and 4 mm/min for a 50-mm gauge length).

All the specimens underwent brittle fracture at relatively low strains; Figure 5 shows representative stress–strain curves and Table 2 summarizes the results (averages for three specimens), along with results for specimens containing a commercial dimethyl dihydrogenated tallow exchanged MMT. The organically modified clay was mixed with the HBP in THF at 50 °C and stirred for 1 h, giving translucent specimens on drying. WAXS indicated intercalation with a gallery spacing of 3.84 nm, increasing to 4 nm on reaction with MDI. The strength and stiffness in the exfoliated composites increased with respect to the neat matrix, but there was a decrease in strain at break. The specimens containing the organically modified clay showed an increase in both strength and strain at break

Table 2. Mechanical Data for Model Polyurethane Composites

wt % clay	strength (MPa)	modulus (GPa)[a]	strain at break (%)	T_g (°C)[b]
unreinforced	26	1.2	3.0	60.1
2.3% Na⁺MMT	36	2.1	2.3	67.0
4.9% Na⁺MMT	35	2.7	1.8	68.2
2.3% organo-MMT	36	1.5	4.8	62.5
4.9% organo-MMT	33	1.7	3.3	61.8

[a] 1% secant modulus. [b] DSC heating scans at 20 K/min (midpoint of the transition).

(cf. conventional polyurethane elastomers containing intercalated organically modified clays[8]), but the increase in stiffness was smaller than that for the exfoliated composites. Plastification by the organic modifier, which may also react with the MDI, cannot be ruled out. However, any such effect was minor, T_g exceeding that of the unmodified matrix (Table 2). The results are therefore taken to demonstrate significantly enhanced stiffness reinforcement in the presence of exfoliated silicate layers. The versatility of polyurethane chemistry means essentially the same processing route may be used to produce materials with a wide range of properties, including elastomers and glasses. The HBPs are compatible with commonly used poly(ethylene glycol) (PEG) chain extenders, for example, and exfoliated HBP/PEG/Na⁺MMT precursors can be obtained by dispersion in water, again without organic modification of the clay.

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