Synthesis of Polycarbonate-Layered Silicate Nanocomposites via Cyclic Oligomers

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ABSTRACT: A partially exfoliated bisphenol A polycarbonate nanocomposite has been prepared by using carbonate cyclic oligomers and ditallow dimethyl exchanged montmorillonite (B34). Wide-angle X-ray diffraction (WAXD) indicated that exfoliation of this organically modified layered silicate (OLS) occurs after mixing with the cyclic oligomers in a brabender mixer for 1 h at 180 °C. Subsequent ring-opening polymerization of the cyclic oligomers converted the matrix into linear polymer without disruption of the layer dispersion. Transmission electron microscopy revealed that a partially exfoliated structure was obtained, although no indication of layer correlation was observed in WAXD. If linear polycarbonate was similarly treated with B34 in a brabender mixer, only an intercalated hybrid was obtained. Furthermore, conventional melt or solution processing of the B34 with either linear polycarbonate or cyclic oligomers yielded intercalated nanocomposites with interlayer spacings of 3.27 and 3.6−3.8 nm, respectively. These results demonstrate that consideration of molecular architecture (cyclic vs linear) and kinetics (medium viscosity and shear) is critical for nanocomposite formation.

Introduction

The field of polymer nanocomposites is stimulating fundamental and applied research[1−3] because these nanoscale materials often exhibit physical and chemical properties that are dramatically different from conventional microcomposites.[3−5] Research is focusing on layered smectite clays as the reinforcing part of the matrix.[6−21] These polymer-layered silicate nanocomposites can exhibit increased modulus,[6−8] decreased thermal expansion coefficients,[7] reduced gas permeability,[7,9] increased solvent resistance,[10] and enhanced ionic conductivity[11] when compared to the polymers alone. Pioneering work by researchers at Toyota led to the discovery of nanoscale polymer−clay hybrid composites for lightweight materials applications.[2,6,12] By replacing the hydrophilic Na^+ and Ca^{2+} cations of native montmorillonite with more hydrophobic onium ions, they were able to initiate polymerization of ϵ-caprolactam in the interlayer gallery of montmorillonite to form a nylon−clay hybrid. At a loading of only 4.2 wt % montmorillonite, the modulus doubled, the strength increased more than 50%, and the heat distortion temperature increased 80 °C. Several other organic−inorganic nanocomposites based on different polymer matrices, such as epoxy resins,[13−15] polystyrene,[16−18] polyimide,[7] acrylic polymers,[19,20] poly(ϵ-caprolactone),[9] and polyolefins,[21] have also been prepared. Because of the nanoscopic length scale, polycarbonate nanocomposites offer the promise of improved physical properties such as strength, modulus, and scratch resistance without sacrificing optical clarity and toughness.

In general, two idealized polymer-layered silicate structures are possible: *intercalated* and *exfoliated*. The greatest property enhancements are observed for exfoliated nanocomposites. These consist of individual nanometer-thick silicate layers suspended in a polymer matrix resulting from extensive polymer penetration and delamination of the silicate crystallites. In contrast, polymer penetration resulting in finite expansion of the silicate crystallites produces intercalated hybrids consisting of well-ordered multilayers with alternating polymer/silicate layers and a repeat distance of a few nanometers. In practice, many systems fall short of the idealized exfoliated morphology. More commonly, *partially exfoliated* nanocomposites, containing small stacks of 2−4 layers uniformly dispersed in the polymer medium, are obtained. Many times, the layer correlation is not detectable by conventional wide-angle X-ray diffraction (WAXD), and observation relies on transmission electron microscopy (TEM).[22,23] These partially exfoliated structures can be associated with inhomogeneities (size and composition) inherent in the natural smectites or arise from processing factors. Nevertheless, these systems may still exhibit substantial physical property enhancements.

In this study, cyclic oligomers and processing techniques are examined as routes to exfoliated polycarbonate nanocomposites. Bisphenol A polycarbonate can be synthesized from cyclic oligomers by ring-opening polymerization.[24] One important advantage of using cyclic oligomers to prepare polycarbonate is the low viscosity of the cyclic oligomers, which can facilitate reactive processing. Other advantages include no volatile byproducts, better control of molecular weight, fast polymerization cycles, and the potential to prepare functional or block polymers. Additionally, cyclic oligomers are an amenable route to incorporation of inorganic fillers as demonstrated by Cook and co-workers,[25] who prepared macrocomposites using the ring-opening polymerization of polycarbonate cyclic oligomers. We speculate that the low viscosity of these cyclic oligomers may offer unique processing opportunities for the fabrication of nanocompósities, especially with respect to the enhanced mobility of the silicate layers (20−500 nm diameter) in the polymer medium. In this article, we report the synthesis of intercalated and partially exfo-

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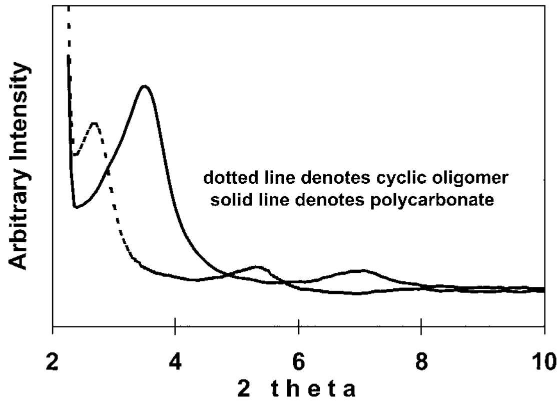


Figure 1. WAXD analysis of samples prepared by solution intercalation of cyclic oligomer and polycarbonate.

liated polycarbonate nanocomposites from polycarbonate cyclic oligomers and an organically modified layered silicate (OLS).

Results and Discussion

For natural montmorillonite, the cations residing in the interlayer space are alkali and alkaline earth metals, and thus the mineral is hydrophilic.[26] This results in a high interfacial tension with organic materials, making the layered silicate difficult to intercalate and disperse homogeneously in a polymer matrix. Therefore, it was necessary to initially replace the hydrophilic, inorganic cations of the native mineral with the more organophilic alkylammonium ions. Specifically, B34 (ditallow dimethyl-exchanged montmorillonite, Rheox, Inc.) was used in this study. B34 was washed with water/ethanol to remove excess quaternary ammonium salt. The B34 OLS displayed an interlayer spacing of 2.47 nm. Depending on the polymer system of interest, different organophilic ions are necessary;[27,28] however, the processing techniques discussed in this work should not be system specific.

Fabrication of an exfoliated nanocomposite requires that the crystallites be disrupted by transport of molecules from the bulk or solution into the interlayer between the silicate sheets. If thermodynamically favored,[27,29] the dispersion of silicate layers and the corresponding mass transport of polymer will be strongly related to the viscosity of the medium. Cyclic oligomers of polycarbonate have significantly lower solution and melt viscosity compared to the corresponding polymer.[30] Therefore, the rate of intercalation as well as the rate of dispersion of the silicate layers should be greater for the cyclic oligomers than for the linear polymer.

Cyclic and Linear Polycarbonate Intercalation. Figure 1 compares the hybrid formation of cyclic oligomers and linear polycarbonate by solution intercalation using wide-angle X-ray diffraction (WAXD). After 5 min of mixing linear polycarbonate and B34 in dichloromethane, little polycarbonate (if any) was intercalated into the silicate interlayers. The basal reflection (d001) was identical to that of unintercalated B34 (2.47 nm). Several hours of mixing was required for the linear polycarbonate to intercalate and swell the interlayer to 3.27 nm. In contrast, intercalation of cyclic oligomers occurred quickly, and the interlayer spacing increased from 2.47 to 3.62 nm. Even when the solvent was removed immediately after the addition of B34 into the cyclic oligomer solution, the cyclic oligomers still rapidly intercalated, leaving no observable basal reflection (d001) of the unintercalated B34. The enhanced rate of absorption of the cyclic relative to the linear polycarbonate may be related to the lower viscosity of the cyclic solution and enhanced diffusivity of the cyclics. Alternatively, the difference in molecular architecture (linear vs cyclic) or the absence of end groups may alter the relative intermolecular interactions at the surface of the OLS, altering the free energy of formation. Differences in intercalation rate relative to molecular weight and intermolecular interactions have been observed previously during melt intercalation.[31,32]

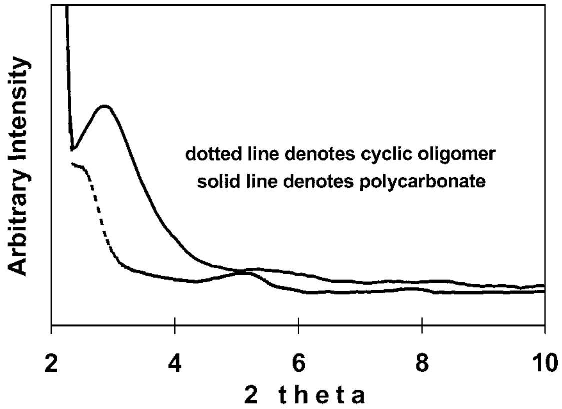


Figure 2. WAXD analysis of samples prepared by melt intercalation of cyclic oligomer and polycarbonate.

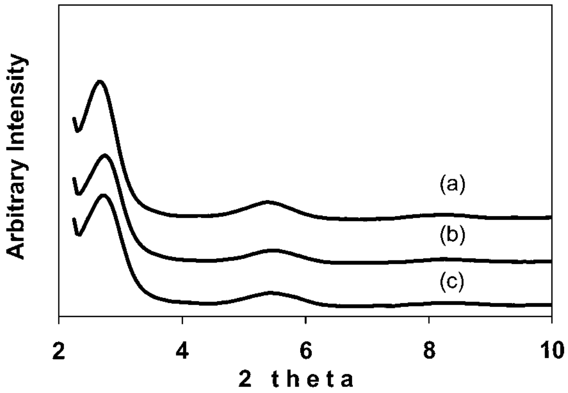
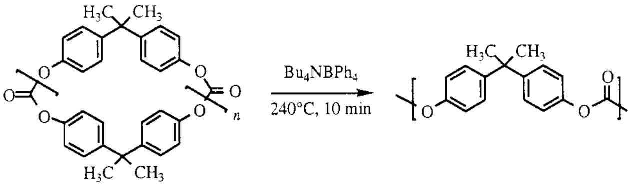


Figure 3. WAXD analysis of samples prepared by melt intercalation by polycarbonate for different times: (a) 1 h, (b) 12 h, (c) 24 h.

As for the final intercalated structure, similar differences between intercalates of cyclic and linear polycarbonate via solution processing were also observed for melt processing. Figure 2 compares WAXD analysis for the melt intercalation of linear polycarbonate and cyclic oligomers at 180 °C. After heat treatment for 1 h, both linear polycarbonate and cyclic oligomers intercalated completely, but to different extents. Prolonged annealing did not result in further increases in interlayer spacing. Figure 3 shows that WAXD pattern of the polycarbonate−silicate composite before and after heating for 1, 12, and 24 h. The cyclic oligomer−B34 intercalate behaved similarly during extended annealing.

Melt intercalation of linear polycarbonate results in a uniform interlayer spacing of 3.27 nm, identical to that previously obtained for polycarbonate intercalation from solution. As with the current study, previous studies have observed that the interlayer spacing is approximately the same regardless of the intercalation method (solution or melt).[28] In contrast, the slightly weaker and broader basal reflections observed with the cyclic oligo-

Scheme 1



mers indicate that the intercalated crystallites are more disordered with an average interlayer spacing of 3.8 nm.

Generally, the equilibrium interlayer spacing of the intercalated linear polymers is associated with a balance of free energy gain associated with increased configurational freedom of the surfactants and free energy loss associated with confinement of the polymer.[27,29] The final intercalated structure has been found to be independent of the polymer molecular weight, which only appears to affect the kinetics of polymer intercalation.[27,31,32] The difference between the cyclic oligomers and the linear polycarbonate is both chemical architecture (cyclic oligomers have a ring structure and no chain ends) and molecular weight. The difference in molecular architecture (linear vs cyclic) and the presence of end groups may alter the relative B34−solvent−polymer interactions, changing the free energy of formation. Thus, not only the rate of hybrid formation but also the final structure is very sensitive to the molecular architecture and associated intermolecular interactions.

Nanocomposite Formation. Since both solution intercalation and melt intercalation of polycarbonate produced only intercalated nanocomposites, ring-opening polymerization of the cyclic oligomers in the interlayer space of the silicate was attempted. We hoped to enhance the disruption of the layers at the molecular level arising from the reaction within the interlayer and growth of a linear polymer. The ring-opening polymerization of bisphenol A cyclic polycarbonate oligomers is an extremely useful method of reactive processing for controlled synthesis of the polymer.[33,34] It produces high molecular weight polycarbonate with a low residual content of cyclic oligomers. Tetraalkylammonium salts of tetraphenylborate are especially useful catalysts for a rapid ring-opening polymerization (Scheme 1).

Initially, B34 was mixed with cyclic carbonate and the initiator (Bu_4NBPh_4) in dichloromethane. After removal of the solvent, intercalation of the cyclic oligomers was observed similar to previously discussed systems without initiator. Because only a small amount of initiator was included (1%, w/w), we assumed that reverse exchange of the tetrabutylammonium cation did not occur and that the initiator was dispersed throughout the system. After annealing a consolidated pellet at 180 °C for 1 h (the purpose of this annealing step was to make a better comparison to samples that are subjected to mixing for the temperature/time conditions), a disordered intercalated structure (broad, weak basal reflection) was formed. Gel permeation chromatography (GPC) analysis indicated that the cyclic oligomers did not polymerize at these temperatures. Polymerization was subsequently carried out at 240 °C for 10 min. However, the ring-opening polymerization did not effect a dramatic distance increase between adjacent silicate layers. Because the initiator was dispersed uniformly in the cyclic oligomers exterior to the interlayer, the extragallery polymerization occurred more rapidly than intragallery polymerization and associated transport of additional cyclics. For static processing (such as this), if the viscosity of the matrix increased rapidly as ring-opening polymerization occurred, exfoliation of the layers would be hindered, and the advantage of using cyclic oligomers to achieve exfoliated nanocomposite is lost. Similar results were obtained on the study of epoxy−clay nanocomposites when extragallery polymerization was faster than intragallery polymerization and only intercalated nanocomposites were formed.[35]

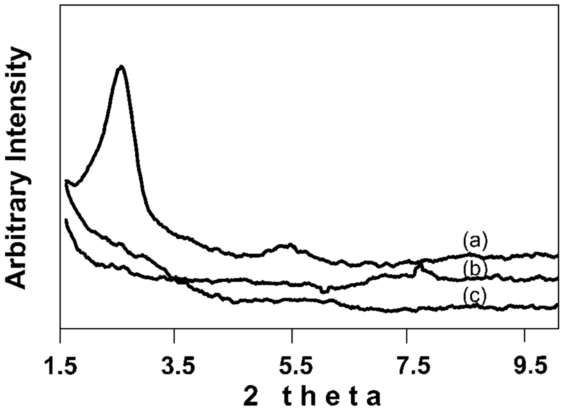


Figure 4. WAXD analysis of polycarbonate−OLS hybrid after annealing a mixture of polycarbonate and OLS B34 in a brabender at 180 °C for 1 h and 240 °C for 10 min (a); after annealing a mixture of cyclic oligomer and OLS B34 in a brabender at 180 °C for 1 h (b); and after annealing a mixture of cyclic oligomer and OLS B34 in a brabender at 180 °C for 1 h followed by polymerization at 240 °C for 10 min (c).

When the cyclic oligomer−B34 hybrid is subjected to polymerization conditions in the absence of Bu_4NBPh_4, a slow conversion of the oligomers to polymer is observed (similar in polymerization rate for cyclic oligomers alone). Because the OLS is modified with alkylammonium cations, one might expect that these organic cations could as suitable polymerization catalysts, analogous to Bu_4NBPh_4. However, we observed very little polymerization unless Bu_4NBPh_4 is added to the hybrid. At this time, we do not know whether this reflects the difference between intra- versus extragallery species or that Bu_4NBPh_4 is a particularly effective catalyst for the ring-opening polymerization.

An alternative processing methodology arises from the assumption that the disordered intercalated structure achieved after an 180 °C anneal is kinetically limited because of the necessity of Brownian motion of the silicate layers without the addition of shear mixing forces. Thus, applying a shear force should decrease the hybrid formation time by breaking up primary particles and increasing sample uniformity. Figure 4 summarizes the results of incorporating shear into the processing. When a mixture of B34, cyclic carbonate, and initiator was annealed in a brabender at 180 °C for 1 h, an exfoliated cyclic oligomer−B34 hybrid (with respect to WAXD) was obtained (Figure 4b). Heating at 240 °C for 10 min effected ring-opening polymerization of the cyclic oligomers. WAXD analysis indicated that the exfoliated structure was retained; thus, the ring-opening polymerization converted the cyclic oligomer matrix to linear polymer without disrupting the layer distribution. GPC analysis indicated that a linear polycarbonate with $M_w = 40\,000$ g/mol was obtained. Figure 5 shows TEM of the final product demonstrating the presence of individual layers as well as packets of silicate consisting of 3−5 layers. This is consistent with a partially ex-

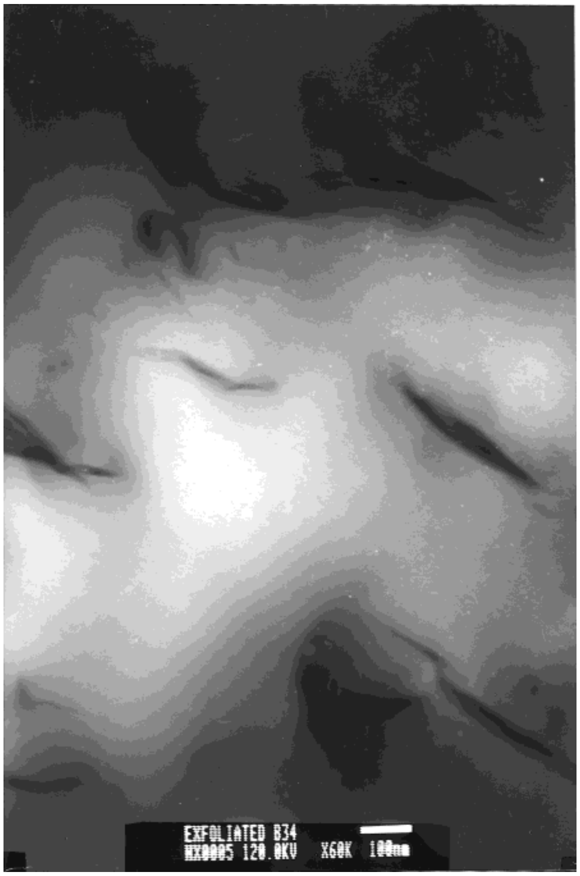


Figure 5. TEM of exfoliated polycarbonate–silicate hybrid obtained by brabender mixing of cyclic oligomer, B34 OLS, and the catalyst Ph_4BNBu_4 followed by ring-opening polymerization of hybrid.

foliated nanocomposite and emphasizes the limitation of only using WAXD in identifying nanocomposite structures.[23]

For comparison, a polycarbonate–B34 mixture was annealed in a brabender using the same process (Figure 4a). In contrast, the resulting polymer–B34 hybrid was an intercalated nanocomposite with the same interlayer spacing as the melt intercalation product produced without shear force applied. Note that FT-IR analysis revealed no significant changes of peaks and their relative intensities after heat treatment, which indicates no significant degradation of either polymer or B34 for these elevated processing temperatures. These observations are consistent with previous studies indicating that the use of shear does not effect the final structure of linear polymer hybrids.[31] Overall, the current difference in final structure related to molecular architecture and application of shear imply these are yet to be understood aspects of polymer-layered silicate blending.

Future studies comparing the final structures and rates of formation for nearly monodisperse polymers of comparable molecular weight but different molecular architecture are necessary. In addition, we are currently studying the physical properties of these partially exfoliated polycarbonate nanocomposites.

Conclusion

A partially exfoliated cyclic oligomer–OLS nanocomposite was obtained by mixing cyclic carbonate and B34 in a brabender mixer at 180 °C for 1 h. Subsequent ring-opening polymerization of the cyclic oligomers preserved the exfoliated structure affording a route to polycarbonate–OLS nanocomposites. An analogous mixing experiment with linear polycarbonate and OLS only produced an intercalated structure. Conventional melt or solution processing of the B34 with either linear polycarbonate or cyclic oligomers yielded intercalated nanocomposites with interlayer spacings of 3.27 and 3.6 nm, respectively. These results demonstrate that consideration of molecular architecture (cyclic vs linear) and kinetics (medium viscosity and shear) is critical for nanocomposite formation. Relative to static annealing and/or the presence of a highly viscous polymer melt, a low-viscosity medium and the application of shear appear to be advantageous in achieving disruption of the silicate structure.

Experimental Section

Materials. Organically modified layered silicate (B34) was supplied by Rheox Inc. Polycarbonate was supplied by General Electric ($M_w = 25\,000$ g/mol), and polycarbonate cyclic oligomers ($M_w = 2000$ g/mol; tetrameric oligomer is the most prevalent) were obtained from The Molecular Optoelectronics Corp. B34 was washed with ethanol:water (1:1, v/v) until no halogen anions could be detected by treatment with $AgNO_3$. All other materials were commercially available and used as received.

Solution Intercalation. A 0.5 g sample of B34 was added to a solution of 10 g of polycarbonate cyclic oligomer (or 10 g of linear polycarbonate) in 50 mL of dichloromethane. After 5 min at room temperature, the solvent was removed in vacuo. The intercalated composite of cyclic oligomer–B34 (or polycarbonate–B34) was dried in the vacuum oven at 50 °C overnight.

Melt Intercalation. A 10 g sample of powdered polycarbonate cyclic oligomer (or polycarbonate) was mixed with 0.5 g of B34. The mixture was pressed into pellets with a hydraulic press and heated to 180 °C in a vacuum oven for 1 h followed by heating at 240 °C for 15 min.

Synthesis of an Exfoliated Nanocomposite. A 5 g sample of B34 and 1 g of tetrabutylammonium tetraphenylborate were added to a solution of 100 g of polycarbonate cyclic oligomer in 500 mL of dichloromethane. After 5 min at room temperature, the solvent was removed in vacuo. The mixture was dried in the vacuum oven at 50 °C overnight. The mixture was added to a brabender mixer and processed at 100 rpm. The temperature was kept at 180 °C for 1 h and then at 240 °C for 10 min. The brabender used in this study was C.W. Brabender PL 2000.

Characterization. Wide-angle X-ray diffraction (WAXD) analysis was performed on Rigaku diffractometer equipped with a rotating-anode generator system using Cu–Kα radiation. Transmission electron micrographs were taken from 50 to 70 nm thick, microtomed sections using a JEM-1200EXII TEM with 60 kV accelerating voltage. Molecular weight analysis was performed with a Waters 510 pump, two Plgel (Polymer Laboratories) mixed D columns (5 u), and a Waters 410 differential refractometer. Molecular weights were calibrated by comparison to narrow MWD polystyrene samples (Polymer Laboratories). Data analysis was performed with the E-Z Chrom software package.

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