Published in final edited form as:

Langmuir. 2008 November 18; 24(22): 13148–13154. doi:10.1021/la8015518.

Nanoparticle-Reinforced Associative Network Hydrogels

Sarvesh K. Agrawal¹, Naomi Sanabria-DeLong², Gregory N. Tew², and Surita R. Bhatia^{1,*}

¹ Department of Chemical Engineering, University of Massachusetts, Amherst, 686 North Pleasant Street

² Department of Polymer Science and Engineering, University of Massachusetts, Amherst, 120 Governors Drive, Amherst, MA 01003

Abstract

ABA triblock copolymers in solvents selective for the midblock are known to form associative micellar gels. We have modified the structure and rheology of ABA triblock copolymer gels comprising poly(lactide)-poly(ethylene oxide)-poly(lactide) (PLA-PEO-PLA) through addition of a clay nanoparticle, laponite. Addition of laponite particles resulted in additional junction points in the gel via adsorption of the PEO corona chains onto the clay surfaces. Rheological measurements showed that this strategy led to a significant enhancement of the gel elastic modulus with small amounts of nanoparticles. Further characterization using SAXS and DLS confirmed that nanoparticles increase the intermicellar attraction and result in aggregation of PLA-PEO-PLA micelles.

Keywords

nanocomposite; biomaterials; laponite; gel; associative polymer

1. Introduction

Physically-associating polymers have been the subject of several studies due to their ability to form networked gels. The “stickiness” or the associative strength of the functional group that forms the network junction points can often be manipulated to modify and control the properties of the physical gel. Common examples of such physical gels are amphiphilic block copolymers in selective solvents,¹ hydrophobically-modified polymers,^{2,3,4} and gels with crystalline domains formed by freeze-thaw procedures.⁵ These materials often have interesting nanoscale structure and rheological properties that can be controlled by small changes in the polymer chemistry or polymer interaction with the surroundings (e.g., through modifying the solvent, adding surfactant or salt, changing temperature or pH, etc.), allowing for the design of materials optimized for a variety of applications.

A common architecture for block copolymer-based physical gels are ABA triblock copolymers, or analogously telechelic modified polymers, in a solvent selective for the midblock.^{1–4,6–8} In dilute solution, the polymers aggregate to form single “flowerlike” micelles. However, at higher concentrations the midblocks bridge between micelles, leading to formation of a three-dimensional network and gelation. The junction points formed are temporary and reversible, and therefore they may break and reform frequently over the time scales a typical rheological experiment.

*To whom correspondence should be sent: sbhatia@ecs.umass.edu.

We have previously studied solutions and gels formed by ABA triblock copolymers in which the A block is crystallizable. Specifically, we have focused on poly(lactide)-poly(ethylene oxide)-poly(lactide) (PLA-PEO-PLA) in water.^{9–18} The biocompatibility of PLA- and PEO-based materials has generated a great deal of interest in PLA-PEO copolymers for biomaterials applications. We have shown in previous work that we can control and modify the structure and properties of these gels by changing the stereospecificity of the PLA block to yield in a network that either has amorphous poly(D,L-lactide) blocks forming the network junction points or semi-crystalline poly(L-lactide) blocks forming the junctions. Using these polymers we were able to design stiff hydrogels with elastic moduli in the range of 1–10 kPa, by changing the crystallinity and molecular weight of the hydrophobic PLA block.

The ability of a material to mimic the mechanical properties of native tissues is an important consideration for tissue engineering applications,^{19,20} and there are some soft tissues with moduli in the range of 1–10 kPa, including the nucleus pulposus of the spinal disk, and the eye lens.²¹ However, several tissues of interest, such as nasal and articular cartilage, are significantly stiffer, with moduli of 10–1000 kPa.^{22–25} It is important to note that these reported moduli for tissues are usually from tests performed in compression, so directly comparing them to the shear elastic modulus is not applicable. Nevertheless, it is clear that a somewhat higher range of elastic moduli, perhaps 2–300 kPa, is desirable for certain soft tissue engineering applications. Thus, our aim in this study is to develop a strategy for creating biocompatible physical gels with elastic moduli greater than 10 kPa for use as cell scaffolding materials in soft tissue engineering.

Our previous small-angle neutron scattering (SANS) studies¹⁴ show that PLA-PEO-PLA in water forms micellar aggregates with an inner PLA core surrounded by a corona of the hydrated PEO blocks. The dimensions of these aggregates were found to be in the range of 20–30 nm. We were able to enhance the elastic modulus of these gels by systematically increasing the hydrophobic PLA block length and forming crystalline PLA junctions. However, as we increased the length of the PLA block beyond a critical value, we could not achieve significant enhancement in elasticity of the gels.¹⁰ Analysis of the rheological data indicated that < 12% the PEO midblocks were acting as elastically effective chains in the network.¹⁰

In associative gels such as these, the fraction of bridging chains is typically set by thermodynamics. Thus, new strategies must be applied to allow additional chains to participate in the network. Here, we present an approach to further modify and control the rheological properties of associative gels by addition of nanoparticles, specifically laponite particles, leading to additional junction points in the network. Laponite clays are disk-like nanoparticles with a diameter of 25 nm and thickness ~ 1 nm; the diameter is on the order of the size of the micelles in our PLA-PEO-PLA gels. Although laponite is a commercial product, it is well-characterized and has been studied as a model discotic colloid.^{26,27} Laponite dispersions have not previously been used in soft biomaterials; however, they have been approved for use in topical applications such as baby creams, cosmetics, skin cleansers, and deodorants, as well as for toothpaste and shampoo, and hence have undergone extensive toxicological characterization.²⁸ Laponite is also approved for use as an agent applied to growing crops and is classified as an “inert” agrochemical,²⁸ and laponite-containing gels have been investigated for use as drug delivery vehicles.^{29–32}

Laponite nanoparticles and related clays have been utilized in several previous studies along with polymers such as poly(ethylene oxide) (PEO)^{33–39} or poly(N-isopropylacrylamide) (PNIPAA)⁴⁰ to form nanocomposite gels with enhanced mechanical properties. In many of these systems, the surface of the nanoparticles provides an interface on which polymers can

physically adsorb, thereby leading to formation of a junction between different polymer chains and eventually formation of a particle-polymer network. The previously cited experimental studies as well as others^{41,42} and recent theoretical work⁴³ have shown that this strategy is effective for mixtures of nanoparticles and adsorbing homopolymers, and a small concentration of particles can lead to a significant enhancement in the elastic modulus. The adsorption of PEO onto laponite surfaces has been confirmed by small-angle neutron scattering and dynamic light scattering.^{44–47}

We hypothesize that the PEO corona of our micelles will adsorb onto the disk-like nanoparticles, leading to additional junction points and formation of gels with enhanced elasticity. This is shown schematically in figure 1. This strategy enables some of the PEO “loops” to become elastically effective chains in the network. It should be noted that even if the clay platelets are not completely exfoliated in such a system, it would still be possible for micelles to adsorb on the faces of stacks of platelets. Thus, by contrast with other nanocomposite work in the literature, we have not focused on the degree of exfoliation of the clay particles. Rather, the present work is an effort to form stiff nanocomposite gels with enhanced rheological properties via the use of two different types of network junctions.

To our knowledge, there have been only a few studies of associative gels containing nanoparticles. A previous study examined various types of nanoparticles in gels of poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) (SEBS).⁴⁸ This work, however, showed only weak property enhancement upon addition of small amounts of nanoparticles. Another group focused on the adsorption of PEO-PPO-PEO micelles onto laponite surfaces, but these studies were done at low polymer concentrations.⁴⁹ Finally, the viscometric properties of dilute laponite dispersions in the presence of hydrophobically modified (hydroxypropyl) guar have been reported.⁵⁰ The latter study indicated that the hydrophobically modified (hydroxypropyl) guar systems associate both through their hydrophobic ends and via adsorption of the hydrophilic parts of the polymer chain onto the clay surfaces. This study was also performed in the dilute regime, and thus it provides little information on the gelation behavior of more concentrated systems.

2. Materials and Methods

2.1 Materials

Either L-lactide ((3*S*)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione) or racemic mixture of D and L-lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) from Aldrich was purified by recrystallization in ethyl acetate and then sublimated prior to polymerization. The α,ω dihydroxy polyethylene glycol macroinitiator with molecular weight 8000 g/mol (PEG 8K, Aldrich) was dried at room temperature under vacuum for two days prior to polymerization. MALDI (matrix assisted laser desorption/ionization) and GPC (gel permeation chromatography) showed this polymer to be 8,900 g/mol in weight. Stannous (II) 2-ethyl hexanoate (Alfa Aesar) was used without further purification. Laponite XLG used in this study was obtained from Southern Clay Products, Inc. (Gonzales, TX).

2.2 Synthesis of PLLA-PEO-PLLA triblock copolymer

PLA-PEO-PLA triblock copolymers were synthesized in the bulk. PEO was weighed into a dry round bottom flask, purged with nitrogen, and placed into an oil bath at 150°C. Stannous (II) 2-ethyl hexanoate was introduced to the molten PEO, followed by the immediate addition of lactide to the macroinitiator/catalyst melt. The flask was capped and allowed to polymerize for 24 hours at 150°C while stirring and was then stopped by quenching in methanol. The product was dissolved in tetrahydrofuran and precipitated in a mixture of cyclohexane and n-hexane. Because the hydrogel rheological properties are extremely

sensitive to the molecular weight of the PLA block^{10,16} as well as any asymmetric or diblock impurities,¹⁸ we repeated the precipitation four times. The copolymer was then dried under vacuum for two days.

2.3 Rheology

To prepare the hydrogels for rheological characterization, a dispersion of laponite in water was first prepared for addition to the polymer. Laponite XLG clay was added to the required amount of nanopure water. The system was then homogenized in a T25 Basic Ultra-Turrax homogenizer for ~ 2 minutes until the clay dispersed completely in water, eventually forming a clear, homogeneous, stable dispersion. The dispersion was then kept at equilibrium for 30 minutes before formation of the polymer hydrogel. This process was followed to ensure that we could get adequate dispersion of clay. Hydrogels were prepared by slow addition of the laponite dispersion to a measured amount of dried polymer sample in order to make samples with total concentration of solids, defined as

$$w_s = \frac{m(\text{polymer}) + m(\text{laponite})}{m(\text{polymer}) + m(\text{laponite}) + m(\text{water})} \times 100, \text{ fixed at 25 wt\%. The concentrations of}$$

laponite that are stated below are defined as $w_L = \frac{m(\text{laponite})}{m(\text{laponite}) + m(\text{water})} \times 100$. The hydrogel samples were kept at equilibrium for 1 day at room temperature and then heated at 80°C for 20 hours. The gels were again allowed to sit for 2–4 days. The final gels obtained were macroscopically homogeneous and translucent in appearance. We have followed this protocol in our previous rheology and SANS studies^{10,14} and we find that this protocol yields samples with reproducible rheology and structure characteristics. As may be expected, the sample rheology and structure depend somewhat on thermal history; this will be described in an upcoming publication.

For rheological characterization, gels were transferred to a TA instruments AR2000 stress controlled rheometer. Rheological measurements were performed using the cone and plate geometry (40 mm diameter cone with a 2° cone angle). A solvent trap was used and water evaporation was not significant for the temperature and timescales investigated. All tests were performed at ambient temperature. In gel systems with slow relaxation times, it is important to ensure that the results are not affected by sample loading. This may either be accomplished through a “preshear” to break the structure or by allowing the structure to equilibrate after loading. We chose not to preshear our samples; rather, after loading, the samples were allowed to equilibrate for 20–30 min before starting any tests in order to minimize any effects of shear during sample loading. We found that this resulting in reproducible data. Stress sweeps at a constant frequency of 1 Hz were first performed to confirm the linear viscoelastic region for collecting subsequent data. Frequency sweep tests over a frequency range 0.01 Hz to 100 Hz were done at constant strain amplitudes of 0.1% to measure G' and G'' (storage and loss moduli, respectively). After frequency sweeps were performed, for select samples we allowed the gels to rest in the rheometer and then repeated the experiments to test reproducibility. Samples recovered and yielded reproducible values for G' and G'' after resting for 20–30 minutes. Because of the highly elastic nature of the gels, we were unable to obtain good data for the viscosity or yield stress of the gels. Under steady shear, many samples tended to yield suddenly into smaller pieces of gel.

2.4 Small Angle X-Ray Scattering (SAXS) and Dynamic Light Scattering (DLS)

SAXS measurements were performed on the hydrogels on a Molecular Metrology SAXS instrument at the W.M. Keck Nanostructures Laboratory at UMass-Amherst. The instrument generates X-rays with a wavelength of $\lambda = 1.54 \text{ \AA}$ and utilizes a 2-D multiwire detector with a sample-to-detector distance of 1.5 m. Samples were sandwiched between kapton films and

this enclosed in an airtight sample holder. This assembly was then put in the X-ray beam path and the data were collected on the samples for 30 minutes.

DLS measurements were performed on an ALV 5000 Static and Dynamic Light Scattering Instrument equipped with an ALV 5000 Multiple Tau Digital Correlator. Experiments were performed at a detector angle of 90°. The samples used for our study were either 0.03 wt% of polymer in water or 0.03 wt% polymer in addition to 0.05 wt% clay nanoparticles in aqueous solution. The samples were prepared by first dispersing polymer in nanopure water to make a 0.03% solution. This solution was stirred for one day and annealed at 80°C for 20 hours to make a homogeneous solution. The solution was then again stirred for two days and was added to a measured amount of clay nanoparticles to make a final solution which had 0.03 wt% of polymer and 0.05 wt% of nanoparticles. The final solution was again stirred for another two days and then kept at equilibrium. All samples were filtered using a 0.45 µm filter prior to measurement and the data was taken after the samples were equilibrated at 25° C. Data was taken on the samples for 1 minute and the measurements were repeated at least five times. The final auto correlation function (ACF) obtained is an average of all the runs taken.

For monodisperse systems, the ACF often follows a single exponential form:

$$g^1(t) = A_1 \exp(-t/\tau_1) \quad (1)$$

However, for more complex systems, a broad distribution of relaxation times is often observed.⁵¹ To take this into account, a stretched exponential function is often used to describe the ACF:

$$g^1(t) = A_2 \exp[-(t/\tau_2)^\beta] \quad (2)$$

The exponent β ($0 < \beta < 1$) is indicative of the width of distribution of relaxation times, with smaller values of β corresponding to a broader distribution of relaxation times.

3. Results and Discussion

3.1 Block copolymer synthesis

The polymers that we used are listed in table 1. We systematically varied two parameters, the length and crystallinity of the hydrophobic PLA block. The polymers with crystalline poly(L-lactic) acid blocks are denoted the L-lactide series polymers, and those made from a racemic mixture of D/L-lactic acid are denoted *rac*-lactide series polymers. Within each series the PLA block lengths have been suitably chosen to match for easy comparison. The sample names indicate the total length of PLA block followed by a letter indicating the stereospecificity of PLA block, e.g., 58R refers to the polymer PLA₂₉PEO₂₀₂PLA₂₉ in *rac*-lactide series with amorphous PLA domains, while 58L refers to the polymer PLA₂₉PEO₂₀₂PLA₂₉ in L-lactide series with crystalline PLA domains.

3.2 Rheology

Figure 2 shows the effect of addition of laponite disk-like nanoparticles to the PLA-PEO-PLA triblock to form nanocomposite hydrogels for 68R, 78R and 82L polymers. As noted in previous publications,^{10,16} the elastic modulus of the neat polymer gels is very sensitive to the molecular weight of the PLA block. In comparing the neat systems with those containing laponite, we see that G' increases dramatically over several orders of magnitude as the amount of laponite in the gel is increased by very small amounts, with the maximum amount

of nanoparticles added being less than $w_L = 2.5$ wt% (corresponding to 1.9% of the total weight of the gel). This dramatic increase in the elasticity of the gels suggests formation of new junctions in the gel by the nanoparticles. The high-frequency elastic modulus of these nanocomposite gels lies in the range of 10–100 kPa, with the concentration of nanoparticles providing another variable besides the crystallinity and length of hydrophobic PLA block to tune the elasticity of the hydrogels. The consistent and monotonic enhancement in the mechanical properties of the gels also suggests that the nanoparticles are well-dispersed within the polymer matrix.

In addition, the hydrogels do not show any loss in elasticity upon addition of laponite nanoparticles. This observation suggests that the underlying polymer network remains intact upon nanoparticle addition, and that addition of nanoparticles does not disrupt the micellar structure. This is corroborated by evidence from SAXS and DLS, as discussed further below.

Addition of nanoparticles also affects the relaxation behavior of the gels, particularly for the *rac*-lactide series. As the concentration of laponite is increased, G' becomes more frequency-independent, suggesting a stiffer and more elastic gel as compared to the neat polymer gel. This effect is particularly prominent in the unmodified *rac*-lactide series gels which display viscoelastic liquid behavior in the neat system, characterized by a power law relaxation behavior at low frequencies and over finite timescales.^{10,52} The frequency where G' and G'' crossover, ω_{int} , defines a characteristic relaxation time of the network, τ_m given

by $\tau_m = \frac{1}{\omega_{int}}$. This relaxation time is related to the average time that a chain takes to dissociate from a junction point, and thus denotes the average lifetime of the crosslink junctions.^{52,53} For the *rac*-lactide series polymers it is clearly seen that the relaxation time of the gels shifts to smaller frequencies, or conversely to longer time scales with addition of laponite, indicating that stronger, longer-lived junctions are formed by the adhesion of micelles on laponite disks. The number density of these junctions increases with increase in laponite concentration. At the highest laponite content of 2.5 wt%, the elastic and loss moduli show critical behavior, with G' and G'' being parallel to each other and following the power law scaling $G' \sim G'' \sim \omega^n$. The behavior of a viscoelastic material at the gel point

can also be described in terms of the loss tangent, $\tan\delta = \frac{G''}{G'}$. At the gel point the value of $\tan\delta$ is independent of frequency.⁵⁴ Before the gel point the value of $\tan\delta$ is known to decrease with increasing frequency, and above the gel point, $\tan\delta$ increases with increasing frequency. Figure 3 shows the change in values of $\tan\delta$ for 68R, 78R and 82L polymers. Based on the criteria developed above, we can deduce from figures 3(a) and (b) that the *rac*-lactide series polymer gels change from a liquid-like response to critical gel behavior and eventually to viscoelastic solid behavior with increase in concentration of laponite. The L-lactide series polymers, on the other hand, display only a viscoelastic solid response even without the addition of laponite because of the presence of crystalline PLA junctions in the gel (figure 3(c)). Thus, the effect of laponite to this system is primarily to increase the elastic modulus of the L-lactide series gels, without significantly impacting the relaxation behavior.

3.3 Small Angle X-ray Scattering

In order to probe changes in the nanoscale structure of the hydrogels upon nanoparticle addition, we performed SAXS experiments. We have previously performed SANS characterization on PLA-PEO-PLA solutions and hydrogels.¹⁴ We have seen that the *rac*-lactide series polymers form spherical micelles in aqueous solution with a core-corona structure where the PLA domains form the core and the corona is composed of hydrated

PEO domains. The L-lactide series polymers form disk-like micellar aggregates with a core composed of crystalline PLA chains and a hydrated PEO corona.

Figures 4(a) and 4(b) show SAXS spectra for 25 wt% gels of 68R and 78R polymers respectively, with and without addition of laponite. As discussed below, the scattering contains contributions from both the laponite particles and the polymeric micelles, making it difficult to quantitatively fit the spectra to models. However, we can gain some qualitative insight into the structure. The scattering data for *rac*-lactide series polymers (figure 4a) shows a peak in the scattering intensity, similar to our earlier SANS spectra on the neat polymer systems.¹⁴ This peak still remains upon addition of the nanoparticles; however the peak position shifts to higher q values. Thus, addition of nanoparticles does not disrupt the micellar assembly of the PLA-PEO-PLA copolymers.

Laponite dispersions at concentrations similar to our systems typically do not show a correlation peak.⁵⁵ Thus, we attribute the peak in our spectra to micelle-micelle correlations. With this, we can estimate an average intermicellar distance d from the

scattering peak position ($q_{\max}$) via $d = \frac{2\pi}{q_{\max}}$. For both 68R and 78R gels the value of $q_{\max}$ shifts to larger q values or inversely to smaller intermicellar distances as the concentration of nanoparticles is increased. This suggests that the nanoparticles effectively increase intermicellar attractions and bring micelles closer together. This increasing attraction could either be from the formation of clay-polymer bridges (figure 1) or from a depletion attraction caused by the particles. However, since the particles and micelles are similar in size, any depletion effects would be small. This provides support for our hypothesis that the particles participate in the network and provide additional junction points via adsorption of PEO chains from different micelles.

The effect of scattering from the laponite particles starts to affect the spectra of the *rac*-lactide polymers in the mid- q range (figure 4a and 4b). The calculated slopes of the scattering spectra in the mid- q region are indicated in the graph for systems with different laponite content. The slope of the spectra increases from -4 to -2 as the laponite content in the system increases. A slope of -4 is expected for three-dimensional objects with sharp interfaces, whereas a slope of -2 is seen for two-dimensional objects with sharp interfaces; deviations from this value towards higher values occur as the interface becomes more diffuse. Disk-like shaped laponite particles are expected to show a slope of -2 in the mid- q region. Inorganic laponite particles scatter more strongly in X-ray than the polymer itself and therefore have a more significant effect on the mid- q region of the scattering spectra compared to the polymer, even though their concentration in the system relative to the polymer is low. In the low- q region, however, the scattering from laponite dispersions at concentrations similar to ours is independent of q and is therefore not expected to affect the scattering peak, which is formed only due to the correlation between the spherical micelles formed by the triblock copolymer.

As mentioned earlier, the L-lactide series polymers form polydisperse disk-like “lamellar micelles.” Because these two-dimensional lamellar micelles are polydisperse and randomly oriented in the gel, a broad shoulder is seen in the low- q region, rather than a well-defined correlation peak. Thus, it is difficult to observe any change in intermicellar distance upon addition of laponite (figure 4(c)). However, even in this case, the mid- q region shows an increase in the value of the slope from -4 to -2 with increase in nanoparticle content.

It is possible that some of the PLA chains may also adsorb to the laponite surfaces. However, in this case, we would expect to see some disruption of the micelle structure. Our SAXS data do not show any evidence of this. In addition, the laponite particles are designed

for aqueous environments, and we do not expect that they will be accessible to the hydrophobic PLA cores. Previous studies on nanocomposites of related clays with poly(L-lactic acid) suggest that more hydrophobic organoclays must be used to obtain interactions of PLA clays with clays.^{56–58}

3.4 Dynamic Light Scattering

If our physical picture is correct, addition of laponite particles to dilute solutions of PLA-PEO-PLA micelles should also increase intermicellar attraction, leading to aggregation of polymer micelles. DLS was used to test this idea. The single exponential function (eq. 1) fit the ACF very well for all systems without nanoparticles, indicating that these systems form monomodal micellar aggregates. However, samples with added nanoparticles required a stretched exponential (eq. 2) to fit the ACF. As mentioned earlier, a stretched exponential dependence of the ACF is associated with a distribution of relaxation times, which in the polymer-nanoparticle system shows the presence of polydisperse aggregates.

Table 2 shows the mean hydrodynamic radii and, for the samples containing nanoparticles, the exponent β for samples containing 0.03 wt% polymer and either no laponite or 0.05 wt% laponite. Similar to our SAXS data, the DLS data represents scattering from both the laponite and the polymer micelles, with the laponite particles scattering more strongly than the polymer chains. In addition, the hydrodynamic radii for the samples with nanoparticles must be taken as estimates only, as these samples have a wide distribution of sizes, and the mean size may not be truly representative of the sample. Nevertheless, some observations can be made. The hydrodynamic radii for the samples with no laponite agree well with estimates of the micelles radius obtained from SANS,¹⁴ 20–30 nm. As expected, the hydrodynamic radii are somewhat larger than the thermodynamic radii given by SANS. For all polymers, the mean aggregate size increases at least three times upon addition of laponite. Scattering from laponite particles at concentrations near 0.05 wt% shows only individual particles, roughly 30 nm in size, and no particle-particle aggregates.⁵⁵ Thus, the large values for R_h we obtain must represent aggregates of polymer micelles caused by addition of the laponite particles. This is consistent with our earlier hypothesis.

4. Conclusions

We have shown that clay nanoparticles can be used to enhance the elasticity of PLA-PEO-PLA hydrogels. Our SAXS and DLS data suggest an increase in the strength of attraction and degree of aggregation between PLA-PEO-PLA micelles when laponite particles are added. This intermicellar aggregation leads to an increase in the number of physical crosslinks in the gel, which in turn leads to physical gels with enhanced elastic moduli. An increase of almost an order of magnitude in elastic modulus was observed with relatively small amounts of added laponite.

We have used a commercial nanoclay that is known to adsorb PEO for these studies. An interesting extension of this work would be to create systems with nanoparticles whose surfaces had been specifically tailored to interact with either the PEO or PLA block. Nevertheless, we believe our studies show proof-of-concept that this strategy can be used to enhance the elasticity in associative polymer gels.

The elastic modulus of these hydrogels is in the range of several soft tissues, which is favorable for tissue engineering applications. Again, although laponite itself has not been used in soft biomaterials, we believe that our studies could provide motivation for examining the biocompatibility of clay-based systems as well as developing biocompatible nanoparticles that could be used in a similar fashion.

Acknowledgments

This material is based upon work partially supported by the National Science Foundation under Grant No. DMI-0531171. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. Support for this work was also provided by a 3M Nontenured Faculty Award and Dupont Young Professor Award to S.R.B.; and an NIH Fellowship to N.S.D. and a fellowship from the University of Massachusetts to S.K.A. as part of the Chemistry-Biology Interface Training Program (National Research Service Award T32 GM08515). This work also utilized central facilities of the NSF-sponsored MRSEC on Polymers (DMR-0213695).

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Figure 1. Schematic of structure in the nanocomposite gels upon addition of disk-like laponite nanoparticles for (top) *rac*-lactide and (bottom) L-lactide copolymers. In addition to the junctions formed by hydrophobic PLA, PEO-clay interactions form additional junction points.

Figure 2(a).

Figure 2(b)

Figure 2(c)

Figure 2.

Effect of addition of laponite nanoparticles on G' (filled symbols) and G'' (open symbols) of hydrogels of (a) 68R, with 0.0 (inverted triangles), 1.0 (triangles), 1.5 (diamonds), 2.0 (circles) and 2.5 (squares) wt% laponite; (b) 78R, with 0.0 (inverted triangles), 1.0 (diamonds), 1.5 (circles), and 2.5 (squares) wt% laponite, and (c) 82L, with 0.0 (inverted triangles), 1.0 (triangles), 1.5 (circles) and 2.5 (squares) wt% laponite. The total weight of solids in all the systems is kept constant at 25 wt%.

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 3. Frequency dependence of $\tan \delta$ for (a) 68R (b) 78R (c) 82L polymer gels at 25 wt% concentration.

Figure 4(a)

Figure 4(b)

Figure 4(c)

Figure 4.

Effect of addition of laponite nanoparticles on small angle X-ray scattering spectra of hydrogels of (a) 68R (b) 78R (c) 82L polymers. For each figure, the curve with the lowest intensity is the sample with no laponite, with the concentration of laponite increasing for each curve at higher intensity. This increase in intensity is to be expected from the heavier inorganic atoms in the laponite particles. The shift in peak position towards larger q values upon addition of laponite is demonstrated by the dashed lines in the graph.

Table 1

Characteristics of PLA-PEO-PLA triblock copolymers synthesized.

Sample Name	DP _{PLA}	DP _{PEO}	MW	Crystallinity of PLA block
58L	58	202	13.0K	crystalline
63L	63	202	13.4K	crystalline
82L	82	202	14.8K	crystalline
56R	56	202	12.9K	amorphous
68R	68	202	13.8K	amorphous
78R	78	202	14.5K	amorphous

Table 2

Mean hydrodynamic radii and stretched exponential factor obtained by fitting the DLS data to eqs. (1) and (2).

	0.03 wt% polymer	0.03 wt% polymer, 0.05% laponite	
	R_h, nm	R_h, nm	exponent β
56R	13.0 ± 0.1	43.7 ± 0.1	0.90
68R	30.7 ± 0.5	321.8 ± 4.1	0.55
78R	32.8 ± 0.4	89.9 ± 0.4	0.77
58L	28.9 ± 0.3	141.9 ± 0.4	0.34
63L	46.7 ± 0.2	221.7 ± 1.5	0.24