RHEOLOGICAL PROPERTIES OF A MODEL SOFT SOLID NANOCOMPOSITE

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RHEOLOGICAL PROPERTIES OF A MODEL SOFT SOLID NANOCOMPOSITE

A Dissertation Presented
by
VIJESH A. TANNA

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements of the degree of
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Polymer Science and Engineering
RHEOLOGICAL PROPERTIES OF A MODEL SOFT SOLID NANOCOMPOSITE

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ABSTRACT

RHEOLOGICAL PROPERTIES OF A MODEL SOFT SOLID NANOCOMPOSITE

SEPTEMBER 2018

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The fabrication and physical properties of polymer/clay nanocomposites has received a great deal of interest in both academic and industrial settings. Clay is a natural 2D mineral comprised of stacks of platelets with high aspect ratios held together through electrostatic interactions. Typically, polymer/clay composite are found to have the best physical properties when these clay sheets are randomly dispersed, exfoliated, throughout the polymer matrix. However, achieving this state is non-trivial due to the strong electrostatic forces holding the clay sheets together. Previous work has shown by mixing an end-functionalized, hydroxyl or carboxyl terminated, polybutadiene with clay, exfoliation can be achieved with mild annealing, which our group has termed the “self-exfoliation” process. The exfoliation of clay leads to the polybutadiene/clay composite forming a soft solid physical gel, presenting a model soft solid to study a material near its gel point. The work presented here relies on using the self-exfoliation process as a model material platform for 4 projects: (1) yielding of the soft solid physical gel, (2) understanding the effect of clay platelet size on the composite’s linear viscoelastic
properties, (3) modification of the polymer to tune its interactions with the clay filler and (4) crosslinking of the polymer matrix to create a clay filled thermoset.

In the first project, the yielding behavior of the polybutadiene/clay physical gel was studied. Shear yielding was performed by exposing samples to large amplitude oscillatory shear (LAOS) above their yield stress/strain. These large stresses/strains decrease the composite’s modulus and increase its characteristic relaxation times causing an irreversible softening and reduced the material’s internal connectivity. Samples were exposed to SAOS-Deformation-SAOS (SDS) sequences in which deformations were applied by increasing the deformation strain amplitudes and duration, followed by linear viscoelastic characterization through small amplitude oscillatory shear (SAOS). The flow-induced structural changes first began to occur at the same stress/strain values as the onset of non-linearity in traditional SAOS to LAOS (StL) stress amplitude sweeps. Yielding was found to be a strain activated process since the onset of non-linearity is independent of both frequency and temperature with respect to strain, not stress, amplitude. Finally, SDS measurements were performed at increasing deformation times and showed that these flow-induced structural changes require time to occur and soften the material through a reverse gelation type process.

In the second project, we investigated the role of platelet size on the viscoelasticity of the same nanocomposite. Here two liquid polybutadienes served as matrix fluids, a non-functionalized polybutadiene (PB), which is a non-interacting liquid, and a carboxyl terminated polybutadiene (CTPB), which caused the clay to exfoliate. Un-exfoliated clay particles were suspended in PB and the liquid mixture was treated with high-intensity chaotic flow in a planetary mixer to reduce the clay platelet size. After performing the size-reduction, clay particles were then exfoliated through the addition of CTPB. The exfoliated
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The third project explored performing post-polymer modification on polybutadiene to vary the location and number of functional groups on the matrix. Prior work on the self-exfoliation process had been limited to commercially available end-functionalized polybutadiene. Thiol-ene click chemistry was used to vary the hydroxyl groups content in the polymer matrix. The addition of hydroxyl groups increased the polymer’s glass transition temperature and as a direct consequence, increased the modulus and other linear viscoelastic functions. Composites were formed by adding clay to the synthesized polymers. Interestingly it was found that exfoliation and physical gelation still occurred when having only a single hydroxyl group per chain (on average). While the composites fabricated with the highly grafted polybutadiene exhibited a lower modulus and remained in a swollen intercalated state due to a lack of mobility. The findings presented here describe the self-exfoliation process as two separate steps: intercalation, driven by the presence of functional groups, and exfoliation, driven by having enough overall mobility in the system.

In the final project, a polybutadiene/clay thermoset was developed using the self-exfoliation process. Sample fabrication was designed using a one-step mixing process to allow clay exfoliation to occur first via mild thermal annealing followed by UV activated
chemical crosslinking of the polybutadiene's double bonds. By achieving a high
crosslinking density, the composite's storage modulus was shown to increase by several
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only at high frequencies, in which the response was dominated by the elasticity of the
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CHAPTER 1
INTRODUCTION

1.1 2D Materials and Applications

Nanocomposites have received a great deal of interest in both academic and industrial settings due to the added benefits the particles can provide to a polymer matrix (Balazs 2013, Hussain 2006, Schadler 2007). A standard grouping of particles is based on their shape: 1D (rods/fibers), 2D (platelets) or 3D (spheres) (Kalfrus 2007). Characterization of asymmetric particles can be more challenging due to their different dimensionalities. The focus of the work presented here is on high aspect ratio 2D nanoparticles. Two dimensional nanoparticles have a broad range of applications stemming from their high aspect ratio (large surface area relative to their thickness) and high effective volume fraction at relatively low loading. Examples of such materials include but are not limited to barrier/membrane properties, conductivity, and mechanical reinforcement.

Barrier properties of 2D particle/polymer composites have been studied extensively because of their ability to increase the diffusive path a molecule (gas or liquid) must take when passing through a barrier even at relatively low loadings (Kim 2010, Bharadwaj 2002, Lu 2005). An extension of this is porous 2D particles (such as zeolites) which can be used for high-flux membrane separation applications, with their selectivity being dictated by the pore size (Kim 2013). Materials such as graphene and MoS$_2$ have shown remarkable promise in the semi-conductor industry due to the particle’s conductivity along a sheet (Zang 2005, Splendiani 2010). Single sheet 2D fillers such as graphene and nanoclays have also been added to polymeric solids to
improve the materials overall mechanical properties, especially fracture toughness. This relies upon having the crack propagation distance increase relative to the unfilled polymer counterpart (Chandrasekaran 2014). Finally, single sheet 2D materials have also been added to liquid polymers (polymer solutions or polymer melts) to create percolating, soft solid networks which provide significant modulus increases (Kim 2010, Krishnamoorti 1997). When single sheet 2D sheets are achieved, the percolation threshold can be achieved at relatively low loadings compared to 1D or 3D particles due to the high effective volume occupied by the sheets. The focus of this work is to use these 2D materials for mechanical reinforcement, focusing on nanoclay.

1.2 Montmorillonite and Organically Modified Montmorillonite Clay

Clay is a layered natural mineral which falls within the class of phyllosilicates. This class of materials refers to those containing an ABA layering, specifically comprising of two tetrahedrally coordinated sheets of silicon and oxygen atoms, silicate layers, sandwiching a strongly bound octahedral sheet of a metal oxide (Ray 2003). The most commonly studied clays are montmorillonite (MMT), saponite, and laponite all of which have the above-mentioned ABA structure but vary in terms of the chemical composition and dimensionality. Specifically, MMT clay consists of two tetrahedral sheets of silicate, sandwiched between aluminum oxide, Al₂O₃. At random positions throughout the sheet, the aluminum is substituted for other metal oxides such as iron oxide or magnesium oxide. This results in the middle metal oxide layer adopting a net positive charge. As a result, the outer silicate sheets have randomly distributed negative charges which are balanced by counterions, typically sodium, which rest in between the clay sheets. These charges make MMT hydrophilic and results in strong cohesion forces which hold the
sheets together. Figure 1.1 shows the chemical structure of MMT clay described above. The lateral dimensions of MMT sheets are approximately 1 micron in both length and width. This allows MMT to be treated as a stack of 2D platelets with a 1.1nm spacing between the clay sheets. While these values provide nice approximations, there is a great deal of variation based on the source of the clay. For instance, the amount of substitution (governing the charge on the material), the number stacks per clay sheet, and the lateral dimensions of the clay sheet all change based on the source of the clay.

![Figure 1.1: The chemical structure of MMT clay in which counterions are found between the clay sheets to help stabilize the negative charges from the silicate layers reproduced from Grim (1962).](image)

Experimental techniques have been established to quantify the differences that may exist between MMT based on the clay’s source. Cation exchange capacity (CEC) is an experimentally measured value used to quantify the amount of charge present on a charged species. This value is determined by either titration, liquid/gas absorption, or zeta potential (Hang 1970). Another key parameter is the average number of platelets that make up a given clay particle which has been reported to be anywhere between 10-150 platelets (Marchant 2002, Fornes 2001). Measuring this value is difficult and is done by either counting the number of platelets per stack based with TEM images or using fitting
functions to fit x-ray scattering profiles. Another common difference among different MMT is the sheet’s lateral dimensions which depend more upon the processing of the mineral. While a fair amount of literature has been established regarding characterization of clay, it still remains a challenging process.

Due to the hydrophilic nature of MMT clay, it has limited compatibility with most commercial polymers which tend to be hydrophobic, particularly polyolefins. To improve the clay’s compatibility, a cation ion exchange method was developed in which the clay’s sodium counterion could be exchanged with an organic cation (Sposito 1985). Once the sodium counterion is replaced, the MMT is referred to as organically modified montmorillonite (oMMT) clay. This process has been well developed to the point where organoclays can now be purchased commercially with a variety of different substituted organic cations suitable for different polymer matrices. The most standard cation used is an alkyl ammonium chloride salt with sodium chloride being the byproduct from the exchange. The exchange requires multiple washing cycles to ensure all the inorganic counterions have been replaced with the organic counterion.

The development of commercial organoclays simplified the process of fabricating polymer/clay composites. One key benefit of the organic cation is that the alkyl tail can be replaced with any R group to make it compatible with a given polymer. For example, the R group could be anything from an alkyl tail to an ethylene glycol chain, or a PDMS oligomer. In addition to improving the chemical compatibility, the exchange also increases the clay’s sheet to sheet spacing from anywhere between 1-4 nm, depending on the size of the cation. The combination of the increased spacing along with compatibility
of the organic cation with the polymers improves the dispersibility of the clay within a polymer.

1.3 Morphology and Characterization Polymer/Clay Nanocomposites

Polymer/clay composites are fabricated when mixing the two components together. There has been a large amount of research devoted to finding effective methods to process these composites which will be reviewed in the next section. We will first address the microstructure of polymer/clay composites. Once the polymer and clay are mixed, the composite’s structure can be categorized as either being micro-phase separated, intercalated, or fully exfoliated (Figure 1.2). In the micro-phase separated state, the clay maintains its original sheet to sheet spacing, meaning the polymer and clay are non-interacting. Rheologically, this state can be treated as a non-interacting suspension of particles within the polymer matrix and follows the Stoke-Einstein relationship (assuming the clay can be treated as spherical particles). Due to having no favorable interactions between the two components, micro-phase separation results in very slight mechanical reinforcement stemming from the stiffness of the clay filler relative to the polymer. This implies the enthalpic forces between the clay sheets (electrostatic) and polymer-polymer interactions are greater than the enthalpic penalty arising from the phase separation. When the clay is intercalated, it indicates the spacing between the layered sheets has increased but there remains some overall characteristic spacing and structure in the clay. The change in the clay’s spacing typically implies there is some favorable interaction between the polymer and clay (or counterion if substituted) which drives the two to interact. Intercalation is characterized as an increase in the clay’s spacing which can reach as high as 15nm. The final morphological state is exfoliated, in
which the clay is fully dispersed throughout the polymer matrix. This is driven by a combination of both enthalpic and entropic free energy gain from the favorable interactions plus the random dispersion of the single sheets. This state is the most desirable for most applications described previously, because of the large effective volume the sheets occupy relative to it in its stacked form in the microphase separated state. This is especially true when evaluating fluid and solid mechanical properties such as rheology, tensile testing, or DMA.

![Diagram of polymer clay composite states](image)

Figure 1.2: Pictorial representation of the illustrating the three morphological states which exist for polymer clay composite: micro-phase separated, intercalated, and exfoliated.

Characterization of a polymer/clay composite’s microstructure can be determined by scattering (neutron and x-ray), TEM, or AFM with x-ray scattering being the most commonly used. However, each of these techniques have their individual merits and limitations which will be addressed here. We will limit our discussion of scattering to just x-ray scattering here. Both SAXS and XRD can be used with SAXS being more sensitive. The benefits of x-ray scattering are that it can be performed on a fairly large sample volume with a simple standardized sample preparation. However, the drawback of the technique is that it is not sensitive enough to determine the difference between single sheet versus double/triple sheets. Many times, complex fitting functions are used to try and provide more accurate results, but different models and approaches are used
which make this a non-trivial method (Kroon 1998). Both TEM and AFM can be used to physically measure the individual sheets. A typical way of preparing a sample is to separate the clay from the polymer matrix and then to spin coat/drop cast a solution of clay/solvent onto a substrate (microtoming for TEM can also be used). Due to the high aspect ratio of the platelets, it is assumed that the sheets will lay flat on the substrate and are not modified during sample preparation. Both AFM and TEM can only be performed on a small sample volume. It is assumed assume that the volume is representative of the bulk sample. Both techniques also require a great deal of sample preparation and optimization to obtain meaningful data. Many detailed studies focused characterizing the morphology of composites use a combination of these techniques to accurately characterize the material (Causin 2005, Koo 2003).

1.4 Processing of Polymer/Clay Nanocomposites

As previously highlighted, polymer/clay nanocomposites have received a great deal of interest due to clay’s ability to reinforce a polymer matrix. A series of papers from the Toyota research center initially sparked the interest in the field of polymer/clay nanocomposites (Usuki 1993, Usuki 1993, Kojima 1993). In their series of studies, oMMT was successfully intercalated into a nylon matrix by polymerizing ε-caprolactam at 250°C for 6 hours. More interestingly, was the fact that the tensile modulus of the composite was found to increase by 3-fold at only 6wt% loading. Consequently, the number of polymer/clay composite systems has grown substantially with a 2003 article by Ray and Okamoto citing over 80 types. The processing of these composites can loosely be divided into three categories of solution, in-situ polymerization, and melt processing.
Solution processing can be performed in both aqueous (with MMT) and non-aqueous (oMMT) media depending on the polarity of both the polymer and clay. The concept here is to use the solvent to either intercalate or exfoliate the clay along with solubilizing the polymer, and finally subsequent solvent evaporation. One example of this was developed with PVA/clay solution which was found to enhance both the thermal and viscoelastic properties of the composite once the water was evaporated (Ogata 1997). Additional water-soluble polymers have been investigated such as hyper-branched polyester (Plummer 2002) and PEO (Aranda 1992). In all these methods, MMT is mixed with a water-soluble polymer which results in the final structure being either intercalated or exfoliated. However, this is inherently limited to water soluble polymers. Similar experiments have also been performed with oMMT (after performing a cation exchange) in different liquid media and different polymers. The concept remains the same, but a larger library of polymers can now be accessed. Examples of this include poly(e-caprolactone) (Jimenez 1997) and poly(l-lactide) (Ogata, Jimenez 1999) which were processed in chloroform. In addition, a polyethylene/clay composite have also been prepared in a co-solvent system containing xylene and benzonitrile through solution blending (Jeon 1998). The number of polymer/clay composites fabricated by solution processing to intercalate/exfoliate clay is constantly growing and only select studies have been highlighted here. For most applications in this section, the solvent was evaporated, and then the physical properties of the composite were explored. In this way, the solution media is the reason the clay is intercalated/exfoliated and also helps to homogenise the overall solution. A number of physical properties can be altered through the addition of
the clay fillers to a polymer matrix such as thermal transitions, mechanical properties, and morphology which is the motivation for the above-mentioned studies.

The second commonly implored method to fabricate polymer/clay nanocomposites is in-situ polymerization. This process relies upon a monomer diffusing in between the clay sheets, which is then polymerized to increase the chain length and in turn intercalate or even exfoliate the clay. The first example was already discussed when e-caprolactam was used to intercalate the clay (Usuki 1993). Another study used chain-growth polymerization to synthesize PMMA and PS composites by using ultrasonication to allow the monomers to diffuse in between the layered structure (Okamoto 2000). This platform was later extended to form random co-polymers by copolymerizing various monomers (Okamoto 2000). Additionally, polycondensation reactions have been performed to form urethane bond linkages with difunctional monomers (Wang 1998) While only select studies have been highlighted here, several others synthesized thermoplastics and thermosets/clay nanocomposites (Ray 2003, Pavlidou 2008).

The final method used to traditionally fabricate polymer/clay composites is melt processing. This process can be advantageous because its eliminates the need of having small molecules, either solvent or monomers, present in the system for clay intercalation/exfoliation to occur. Typically, a thermoplastic and clay are mixed and subjected to large stresses to force the two components to interact. The first example of this was done by melt pressing high molecular weight PS and oMMT at elevated temperatures which caused the clay to intercalate (Vaia 1993). More intense forms of shear mixing have also been used in which oMMT was extruded into a nylon matrix under various processing parameters (Dennis 2001). The composite with the highest
modulus was extruded using a counter rotating twin screw extruder. This was also the only technique found to achieve full exfoliation of the clay. Variations of these methods have also been explored. In one study, a clay/water slurry was extruded with a nylon matrix. The water in this case is simply acting as a carrier for the clay. Once the slurry came into contact with the high temperature nylon, it began to evaporate which left the exfoliated sheets in their dispersed throughout the matrix (Hasegawa 2003). Another variation of this was found when having oligomers present to help compatalize the polymer and clay, particularly with non-polar olefins. In addition, the oligomers help plasticize the polymer matrix. One of the most famous studies utilized maleic anhydride modified polypropylene oligomers when melt processing PP/clay composites to intercalate the clay (Kawasumi 1997). This platform has been widely adopted by many groups with many subtle variations to optimize these interactions.

All of the previously described, fabrication methods discussed above have disadvantages. In the case of solution processing, it requires solvent evaporation and solvent disposal which can be troublesome when not performed in aqueous media. Furthermore, the method in which the solvent is evaporated also can have major consequences on the composite’s final physical properties. In the case of in-situ polymerization, it requires extensive time and harsh reaction conditions to ensure a high enough conversion of polymerization is achieved. Finally, in the case of melt processing, bulky machinery is required and operated at high temperatures, thus requiring a lot of energy. In addition, while treating the polymer, the 2D particle’s lateral dimension may decrease due to them being fractured when exposed to these large forces and lead to less favorable final properties. All of these processing methods have select drawbacks, limit
the feasibility of the readily available filler. Below, we will present a new platform which
relies on a lower energy, solvent free method to combat these and in the process highlight
some of the unique features of the material system.

1.5 Self-Exfoliation Process

In 2004, Sun and co-workers developed a novel method to exfoliate oMMT clay
in a polybutadiene (PB) matrix by just annealing (Sun 2004). Specifically, the PB was
low molecular weight (below the effective entanglement molecular weight) and end-
terminated with either carboxylic (CTPB) or hydroxyl functional groups (HTPB). It is
believed, although not experimentally verified, that the exfoliation process is driven by
hydrogen bonding between the polymer’s polar end groups and the charges on the clay
sheet’s surface/organic counterions that rest in between the sheets (Chen 2005). This is
supported by the fact that if the same annealing conditions were carried out with a low
molecular weight polybutadiene (PB), without any end groups, the clay maintains its
original spacing (Sun 2004, Chen 2005). Full exfoliation has been shown to occur when
annealing for about 8 hours at 80°C (Momani 2016). Seeing as annealing is a fairly low
energy process, particularly compared to traditional methods used above, our group has
termed this the “self-exfoliation process.”

Once exfoliated, the clay sheets stay in its single sheet form, which is to say the
exfoliation is non-reversible (Wang 2006). From a thermodynamic point of view, thermal
annealing provides the energy needed to overcome a free energy barrier, presumably due
to the electrostatic charges between individual clay sheets, to reach a global free energy
minimum. Exfoliation of the clay is driven by both the enthalpic interactions between the
polymer and clay (or counterion) along with an entropic gain of having the sheets
randomly dispersed throughout the polymer matrix. Since PB is unable to exfoliate the clay, both the entropic and enthalpic gain must play a significant role in allowing the exfoliation to occur.

In agreement with previous work, the addition of clay into the PB, introduces major mechanical reinforcement and connectivity. In fact, the addition of clay to either HTPB or CTPB results in the formation of a physical gel at sufficient loading (Wang 2010). The liquid to solid transition, the percolation threshold, occurs at 3wt% (ϕ=1.5%) (Li 2010). Below 3wt%, connectivity is still realized but not enough to form a physical gel, instead it is a reinforced liquid with increased relaxation times and LV elastic properties. The percolation threshold has been shown to vary slightly depending on the organic counterion used (Li 2010). To date, no additional types of clay beside oMMT have been reported to undergo the self-exfoliation process. At all concentrations of clay (up to 20wt%), the modulus of the composite has been shown to continually increase, meaning more and more connectivity is introduced into the system. This has been measured rheologically by an increase in the storage modulus in Figure 1.3. A second critical concentration of 10wt% has also been reported. Above 10wt% (ϕ=4.5%) the clay adopts an intercalated, not exfoliated, state (Zhu 2007, Wang 2009). While not proven, this is presumed to be due to the effective volume occupied by the sheets increasing to the point in which it can no longer be in an exfoliated state. This critical concentration cannot be detected with linear viscoelastic characterization (Figure 1.3), only with morphological techniques such as x-ray. To summarize the above mentioned critical concentrations, a pictorial phase diagram has been constructed in figure 1.4.
Some more recent findings have also provided key information regarding the self-exfoliation process. The first was the ability to use a blend of unmodified PB with HTPB (Wang 2009). Interestingly, it was found that 25 wt% HTPB with respect to PB was sufficient for exfoliating clay and actually resulted in faster exfoliation, despite the number of functional groups (hydroxyl groups) being diluted. A two-step model has been used to describe the exfoliation. First, the HTPB caused clay to intercalate due to its favorable interactions (hydrogen bonding). This is followed by PB diffusing between the clay sheets and eventually leading to clay exfoliation. The diffusion of the PB between
the swollen clay sheets proceed faster because it does not have any interactions with the sheets. It is driven only by entropy. Rheologically, there is very little difference between the linear viscoelastic properties once exfoliation is achieved. The origin of the connectively will be addressed in the next section. A final study worth mentioning was performed by measuring the structure evolution of the composite using time resolved mechanical spectroscopy (TRMS) and time resolved SAXS (Momani 2016). It was found that the majority of the structural reinforcement is realized during clay intercalating, not exfoliating. Intercalation was achieved at relatively short times (<30 minutes of annealing at 80°C). This correlated with the drastic increase in the clay’s sheet spacing increasing from 2.1nm to 9.5nm. Once intercalation occurs, the spacing between clay sheets remains constant (based on SAXS) but a reduction in the peak intensity was seen. This was attributed to the peeling off of individual clay sheets from the stacks of clay particles. After more extensive annealing (8 hrs at 80°C), the peak completely disappears, indicating full exfoliation. It should also be noted that intercalation of clay is observed even at room temperature and introduces major connectivity. A pictorial model each step of this is depicted in Figure 1.5.

The work presented here uses the self-exfoliation process as a platform for both fundamental and applied research studies. The majority of prior literature in this field was focused on understanding the self-exfoliation process. Little thought had been devoted to understanding how this platform could be used to study other key points of interest. Work presented here will draw upon different features of the composite described above.
Figure 1.5: Proposed model of the self-exfoliation process based on the findings presented by Momani and co-workers. We first presume that clay sheets are phase separated when mixed with the polymer. Eventually the polymer diffuses between the clay sheets and causes intercalation. Individual clay sheets then begin to peel off from the stack until full exfoliation is realized.

1.6 Polymer-Particle and Particle-Particle Connectivity

The composites ability to form a physical gel clearly indicates a percolating network spanning across the entire sample forms due to the exfoliation of clay. However, the origin of the connectivity is still unclear. Presumably, it stems from either particle-polymer interactions or particle-particle interactions. Particle-polymer interactions must play a role since it is necessary to have functional groups present (carboxyl or hydroxyl groups) for self-exfoliation to occur. However, this may just be needed for intercalation/exfoliation to being, but not for connectivity observed. Here, we will present both arguments for both based on prior nanocomposite literature.

Typical model systems governed by particle-polymer interactions are carbon black/polybutadiene and silica/PEO nanocomposites. The addition of the polymer-particle interactions introduces additional connectivity and eventually form a percolating network. It has been shown that having spherical nanoparticles on the same order of
magnitude as the polymer (based on its radius of gyration) provide the best reinforcement and percolation can be reached at loadings as low as seven volume percent (Jancar 2010). Percolation could be achieved at even lower loadings when there are favorable interactions between the two components such as hydrogen bonding, electrostatic interactions or Vander Wal forces such as hydrogen bonding between PEO and the hydroxyl groups on a silica particle (Zhang 2002). Favorable interactions lower the percolation threshold by introducing connectivity which arises from polymers forming on the particle’s surface, and then entangling with neighboring polymer chains (Zhang 2002, Cassagnau 2008). Of course, in our system, the percolation threshold will decrease further when working with asymmetric particles such as clay and can explain why the percolation threshold can be reached at 3wt% in our system ($\phi=1.5\%$) (Li 2010). Examples of hydrogen bonding between polymer and clay have been reported and quantified via FT-IR in certain systems (Lee 2003, Tien 2001).

An additional form of connectivity can be seen from particle-particle intercations. In the case of clay, this is driven by the positive charged edges (hydroxyl groups) of the clay compared to the permanent negatively charged surfaces (Lagaly 2003, Tombacz 2004, Tombacz 2006). The edges charge has been shown to vary based on the local environment the clay is in which makes this a difficult value to quantify. interactions. The most famous example of this comes the so called “house of cards” structure which was first reported in a PP/montmorillonite clay nanocomposite (Okamoto 2001). If exfoliated, this structure cannot be measured via x-ray because in both instances the structure’s morphology consists of randomly distributed platelets, instead TEM must be used. Although there is no well-defined experimental proof, the finds from this work,
particularly those presented in chapter 4, suggest this is the origin of connectivity in these composites.

1.7 Soft Solids about the Gel Point

Polymeric materials near or at their gel point are of great interest use, particularly in the fields of adhesives, food science, and biology (Shull 2002, Mezzenga 2005, Avnir 2006). A material’s gel point is defined as the point at which the polymer’s molecular weight diverges to infinity or the point at which a percolating structure spans across a sample (Colby 2003R). Characterization of polymers near their gel points can be challenging due to their sensitive structure and potential lack of solubility (after the system is gelled). A common tool used to characterize soft solids is rheology and will be used extensively in this work. Vilgis and Winter first theoretically described the chemical gelation of monomers summarized in Figure 1.6 (Vilgis 1988). The bond probability is used to describe the extent of reaction. When this value is 0, it indicates all the monomers are unreacted. When the value is 1, all the functional monomers have been reacted, which is almost impossible to achieve experimentally. Below the gel point, \( p_c \), the material is a liquid and can be defined by its viscosity, \( \eta \). As more and more connectivity is introduced into the system (increase in bond probability), the material’s viscosity increases further as do other viscoelastic properties such as the dynamic moduli. However, the sample is still a liquid and governed by Newton’s Law. This of course is well-known to increase the material’s relaxation times. However, once the gel point is exceeded (\( p > p_c \)), the material is now considered a solid. A solid (if purely elastic) is defined its modulus, rather than viscosity, through Hooke’s Law. As the extent of reaction is increased further, the material’s relaxation times become shorter and the
modulus grows. This could be attributed to an increase in crosslink density and decrease in molecular weight between entanglements.

Figure 1.6: Linear viscoelastic properties of soft solids below and above their gel point, $p_c$. $p_c$ marks the percolation threshold. Below the gel point, the material is a liquid and is governed by its viscosity. With increasing bond probability the gel point is exceeded the characteristic material times decay and the characteristic modulus increases. (Winter 2016)

Rheologically, the gel point was first defined in a classic paper by Chambon and Winter (Winter 1986). In their study, PDMS monomers were crosslinked to various extents of reaction and rheologically characterized (Chambon 1985). It was found that a material’s gel point can be rheologically defined by the point at which tan $\delta$ is independent of frequency. This is analogous to the storage and loss modulus having the same scaling exponent with respect to frequency. Contrary to many experimental studies, the gel point cannot be defined by a crossover point between the storage and loss modulus, a drastically oversimplified method some researchers chose to implore (Winter 1987). In fact, single frequency measurements are not sufficient for identifying the gel point. This can simply be explained by the fact that the crossover point is a frequency dependent value. A material’s gel point cannot be defined by a frequency dependent value because it occurs at a specific time, a time at which is independent of frequency.
Characterizing a material around a gel point can be quite challenging because of a material’s delicate structure near this point. A number of different systems have reported very low yield stresses/strains as reviewed by Stokes and Frith (2008). Therefore, determining a sample’s rheological properties near the gel point can be challenging. Many discrepancies between data sets can be seen, perhaps due to sample loading altering the sample’s structure. Many times, researchers will instead apply a “pre-shear” step on the sample in order to establish a uniform starting condition.

1.8 Experimental Overview

1.8.1 Materials

Carboxyl (CTPB) and hydroxyl (HTPB) end-terminated polybutadienes were purchased from Sigma with molecular weights of \( M_n = 4,200 \) and \( M_n = 2,800 \) respectively. In addition, two different non-functionalized PB matrices (high and low vinyl content) were also used with \( M_n = 2,150 \) and \( M_n = 5,000 \) respectively which served as non-interacting polymers. Organically modified montmorillonite clay particles (Fenghong Clay Corporation) (oMMMT) were used as the clay fillers. This was the only clay used in this study to avoid variations in clay sources which may affect results. Prior to purchasing the clay, it had its sodium counterions substituted with octadecyltrimethyl ammonium. 0.2 wt% antioxidant (Irganox B225 from BASF) was added to all samples to minimize degradation of the polymer at elevated temperatures.

1.8.2 Preparation of Polymer/Clay Composites

Previous work has demonstrated that the functionalized polybutadiene/clay nanocomposite forms a soft solid physical gel, with a low yield stain (Tanna 2017). Therefore, it is essential to load the sample in the rheometer before structure formation can
occur. This avoids the sample’s structure being altered, yielded, during sample loading which would affect its linear viscoelastic (LV) response. We utilize the fact that exfoliation requires time. Samples were then quickly loaded into the rheometer between the plate fixtures before any major intercalation/exfoliation occurred. Annealing was carried out at 80°C for 8 hours in the rheometer followed by LV characterization of the composite. This established the initial state of our sample which formed the physical gel from the exfoliated clay.

A typical sample preparation procedure is described here. After massing the polybutadiene, clay, and antioxidant, the mixture was gently homogenized in a FlackTek planetary mixer at 3000 RPM for one minute. This ensured a consistent mixing quality (reproducible rheological properties) without applying large enough stresses which may cause clay aggregates to break. Immediately after mixing, samples were loaded into the rheometer. This step was performed while the polymer/clay mixture was still a liquid, before any significant structure developed. This also allowed us to mold the samples into a cone and plate geometry for rheological characterization. After having loaded the sample, annealing at elevated temperatures was performed to exfoliate the clay. At sufficient enough loadings, this created the physical gel. This standard procedure was used for all samples in this study. Any variations to this procedure will be described in their respective chapters.

The above prescribed method presents a standardized way to generate samples which are unaffected by the mixing and/or by the sample loading into the rheometer. This can be difficult to achieve with soft solid samples because of their sensitive structure. This allowed us to achieve a reproducible starting condition for rheological characterization. Such
samples will be referred to as “virgin” samples since they are free of any prior stress history since the structure was formed in the instrument. This method, developed by our group, represents a unique way to achieve this structure. Another method commonly implored is to pre-shear a sample to wipe away any stress history on the sample. The limitation of using this approach though is it risks yielding the sample, particularly for solids with a yield stress. The discussion of yielding will be addressed in a later chapter since a whole study has been devoted to it.

1.8.3 Mixer

Samples were homogenized in a planetary mixer (FlackTek SpeedMixer DAC 150), which allows gentle mixing. The planetary mixer is essentially a fast spinning centrifuge with the sample holder at a 45° angle, which rotates around its tilted axis while spinning. The combination of gravitational forces at various positions along the mixing arm enables efficient stress application and mixing of the suspension. This was used throughout our experiments to achieve a homogeneous and a well-defined sample starting state. The forces from the mixer were sufficient to ensure the clay was distributed throughout the matrix but there was no damage to the individual sheets.

1.8.4 Chemical Characterization

The molecular weights of the grafted PB were characterized using gel permeation chromatography (GPC) in THF from Agilent 1260 Infinity instrument equipped with an RI detector. PMMA standards were used to calculate the molecular weights. $^1$H NMR spectroscopy was used to quantify the grafting density with a Bruker Avance III HD 500 MHz NMR.
1.8.5 Differential Scanning Calorimetry (DSC)

DSC was performed to determine the glass transition temperature ($T_g$) of the previously described polymers and their composites. Experiments were carried out using a TA Instrument Q200 DSC with nitrogen gas purge flow at 5 mL/min. Different temperature ranges were used for different experiments and will be described in their individual chapters.

1.8.6 Rheology

Rheological measurements were performed on two different stress-controlled rheometers. The two instruments were a Malvern Kinexus Pro+ and a Stresstech ATS. Different plate geometries and experimental procedures were used depending on the sample with the most standard characterization being small amplitude oscillatory shear (SAOS) frequency sweeps. These were performed always performed at a strain amplitude of 0.1% from 0-80°C in 10K increments from $\omega=1$-100 rad/s unless otherwise indicated. Samples were never measured above 80°C due to potential polymer degradation.

1.8.7 X-ray

Medium angle x-ray scattering (MAXS) was used to characterize the spacing between clay sheets using a Ganesha 300 XL SAXS instrument. Samples were exposed to the x-ray source for 180s at a wavelength of 0.154 nm. The sample to detector distance was set to a fixed distance of 0.691m with a 2mm beam stop.
CHAPTER 2

ONSET OF NON-LINEARITY AND YIELD STRAIN OF A MODEL SOFT SOLID

2.1 Introduction

Soft solid materials such as foams, gels, colloids and soft composites, because of their low modulus, can yield when exposed to small stress or strain. Non-linearity of viscoelastic properties also sets in upon small stress/strain. Both phenomena need to be considered and related to each other for a deeper rheological understanding. Lightly crosslinked gels have been shown to undergo a solid to liquid transition when subjected to shear stresses as low as 100 Pa (Venkataraman 1990). A yield stress of similar magnitude has been reported (200 Pa) in a block copolymer/clay composite (Krishnamoorti 2001). Shear induced yielding may irreversibly change the internal connectivity and/or possibly generate alignment of the sample’s constituents. Examples are the shear-induced alignment of block copolymers (Scott 1992, Koppi 1992) or the homogenization of composites.

A material’s relaxation modulus, $G(t)$, describes all of linear viscoelasticity (Boltzmann 1876). The linear viscoelastic (LV) properties are unaffected by the imposed stress or strain as long as the applied stress or strain is small enough. However, a key question, which arises, is how small the applied stress or strain should be? One may also ask how this stress or strain limit can best be measured and by how much its value changes over a given time span or frequency. Defining the most sensitive way to decouple linear and non-linear terms remains a significant challenge because non-linear terms can never be thought of as being perfectly zero but instead as being negligible at low enough strains.
For most viscoelastic materials, the strain limit of linear viscoelasticity is very small, \( \gamma \ll 1 \), and as a consequence higher order terms, which depend on \( \gamma^2 \ll \gamma \), \( \gamma^3 \ll \gamma \), remain insignificant for LV experiments. Viscoelastic material functions which depend on \( \gamma \) dominate over material functions which depend on \( \gamma^2 \) or \( \gamma^3 \). Examples of such higher order terms are the first normal stress coefficient in shear (Laun 1978)

\[
N_1 \sim \gamma^2
\]

(1)

and the third harmonic response to small amplitude oscillatory shear (Hyun 2006, Cziep 2016).

\[
I_3 \sim \gamma^3
\]

(2)

With increasing stress or strain, the square and cube dependent material functions begin to contribute in a more significant manner. Precise measurements and an ideal material system might be able to quantifiably describe and define when the onset of non-linear terms begin to contribute in a significant enough manner.

Oscillatory shear experiments at small amplitude (SAOS) and at large amplitude (LAOS) have been used extensively to characterize viscoelastic properties of liquids and solids, and to detect the onset of non-linearity. SAOS and LAOS experiments can be performed independently of the type of material and will be applied here to a model soft solid.

This experimental study tries to effectively identify the onset of non-linearity for a soft solid model material. Different LV material functions show different sensitivity to large stress or strain. In one set of oscillatory shear experiments, we begin at small strain or stress and steadily increase the amplitude. Such a SAOS to LAOS strain/stress ramp (StL) starts
well below its critical amplitude where a LV baseline is established. The larger and larger stress/strain amplitudes then drive the sample into its non-linear regime. Typically, deviations from the LV baseline identify the critical stress/strain at which a sample enters its non-linear regime. User defined parameters are sampling density and frequency.

For StL experiments, yielding has been defined by the crossover of the storage and loss modulus (Shih 1999), a maximum in stress amplitude (Yang 1986), and/or the turning down of the modulus beyond a critical stress or strain amplitude (Mason 1996). In all such instances, the rheological response is associated with structural changes. However, it is fair to question whether any non-linear deformation has occurred prior to yielding (i.e. onset of non-linearity = yield stress/strain?). The naturally occurring recovery dynamics of most materials make it difficult to argue any of these criteria. In many instances, one of the above mentioned analytical methods is selected to define yielding and used throughout a given study without verifying if any yielding had occurred prior to this assigned value.

Little attention has been devoted to the effect of frequency on yield stress or strain. A change in frequency raises or lowers the LV baseline, and thus may also affect the yielding behavior. For a fumed silica electrolyte gel, the yield stress has been shown to be unaffected by frequency (Walls 2003). However, for hard sphere colloidal glasses and a thermosensitive soft core-shell colloid, the yield strain increased with frequency (Petekidis 2003, Carrier 2009). Both yield stress and strain showed a power law dependence with frequency in soft colloidal glasses of star polymer solutions (Helgeson 2007). The diverse nature of yielding both in terms of types of materials tested and their relationship with key experimental parameters, presents a need for a detailed study in model materials.
The novelty of this research lies in the use of a soft solid material, which irreversibly changes upon exposure to large stress or strain. Such a property was found in a CTPB/clay composite, which is made up of clay that has been exfoliated in a polybutadiene matrix. The material is able to have a quantifiable stress history imprinted upon it. It “memorizes” if it was ever exposed to large strain so that changes can be quantified rheologically. A major challenge was to load the un-exfoliated sample into the rheometer fast enough before it develops its shear-sensitive structure. Exfoliation causes the material to form a physical gel. Exfoliated samples were sheared using a cone and plate geometry for testing the onset of non-linearity through (1) classical monitoring of LV material functions in StL experiments and (2) stepwise increasing the deformation (LAOS stress amplitude/exposure time) in SAOS-Deformation-SAOS (SDS) experiments. SAOS was then used to monitor the LAOS-induced structural changes. We compare the onset of irreversible change (i.e. yielding) to the deviations of rheological material functions from its linear viscoelastic baseline. Once the relationship was established we used StL characterization to define how yielding/non-linearity varied as a function of frequency. Results from this work suggest that yielding of the polymer/clay composite is a strain activated process.

2.2 Experimental

2.2.1 Materials

The soft solid sample in this study consists of the previously mentioned carboxyl terminated polybutadiene and organically modified montmorillonite clay. Samples for this study were prepared with a CTPB/clay ratio of 90/10 wt%. An additional 0.2 wt% of Irganox B225 (BASF) served as antioxidant to minimize degradation of the polymer.
2.2.2 Sample Preparation

As described in the introduction, a general procedure was used to form the stress-free “virgin” samples. This allowed us to establish a well-defined state for all samples. Anytime a sample was yielded, it a new sample was formed unless otherwise indicated. The need for this will be addressed in the results section.

2.2.3 Oscillatory Shear Measurements

The Malvern Kinexus Pro rheometer was used for these experiments with a cone and plate geometry of 40-mm plate diameter and 4º cone angle, was used to achieve uniform shear. All SAOS measurements were carried out at a constant strain of 0.1%. Specific experimental conditions/parameters for the different yielding experiments will be discussed in the results section individually.

2.3 Results

2.3.1 Shear Sensitivity of Soft Solid Structure

SAOS on the “virgin” sample identifies it as a soft solid (physical gel) with a low frequency plateau in the storage modulus, $G'$, (Figure 2.1, circles). In comparison, the lower modulus curves in Figure 2.1 (squares) highlight the effect of shear on the CTPB/clay structure. The same sample had been sheared at large amplitude (LAOS) for a defined period of time ($\gamma=1.5$, $\omega = 1$ rad/s, $T = 25^\circ$C) and afterwards characterized with a SAOS master curve. The drop in modulus and the frequency shift are significant.

Also important is the irrecoverable nature of the composite’s structural change. While keeping the shear-modified sample in the rheometer, the sample was allowed to rest for 5 hours at elevated temperatures and SAOS was repeated. The corresponding storage and loss moduli curves (Figure 2.1, crosses) are practically identical to the measurement
immediately after shearing (Figure 2.1, squares). No noticeable recovery occurred in the LV properties during 5 hours rest. The sample is still a soft solid, but some of the connectivity in the gel had been reduced permanently. In this way, shear effects are imprinted in the sample and can be rheologically quantified. This property is advantageous for the study of yielding as described further below.

Figure 2.1: SAOS of three states of the 90/10wt% CTPB/clay composite - before shear (circles), after LAOS shear (squares), and after having given the sample 5 hours to recover from LAOS (crosses) (Figure 2.1a). For LAOS shear modification, the sample was subjected to $\gamma=1.5$, $\omega=1\ \text{rad/s}$, $T=25^\circ\text{C}$. Dynamic moduli in the temperature range of 0-80$^\circ\text{C}$ at 10K intervals were shifted to $T=25^\circ\text{C}$. The corresponding shift factors are shown in Figure 2.1b.

2.3.2 Critical Stress/Strain Determined by SAOS to LAOS Transition

Oscillatory shear stress ramps (StL) were performed on “virgin” CTPB/clay composites with the objective of finding the stress/strain limit beyond which the sample was driven out of its LV regime. Stress amplitude sweeps from 0.01Pa to 10,000 Pa were performed at 25$^\circ\text{C}$ at 1 rad/s. At each discrete stress, the sample was subjected to the prescribed shear for 40 s with a 20 s equilibration time between each data point. Figure 2.2 expresses the corresponding data using a variety of LV functions. The sampling density
was varied between 3 (Figure 2.2 circles), 10 (Figure 2.2, squares), and 20 (Figure 2.2, crosses) points per stress decade. The time per data point is kept constant which means experiments with high sampling density take a longer time and allow more extensive for structural changes.

LV material functions of CTPB/clay are shown in Figure 2.2. The linear scale amplifies the noise and sample variations (each StL experiment needed a new sample). Within the LV regime, the dynamic moduli gradually decay with stress amplitude, but then drop off quickly beyond a critical stress amplitude due to a sample’s non-linear response. The slight modulus change at low amplitude was always present but could be considered negligible. Stress amplitudes were increased in a stepwise fashion until the LV material functions began to deviate from the baseline. The steps were chosen of constant size on a logarithmic scale.

The soft solid composite of this study exhibits classical shear thinning behavior, typical for polymer melts and solutions. It is a “type 1” material according to the classification of Hyun (2002). Both the storage and loss moduli drop, but the storage modulus begins to decay at a lower stress than the loss modulus and does so at a faster rate, a phenomenon reported for several materials (Salehiyan 2013, Derkach 2015). Surprisingly, the onset of non-linearity seems to depend on sampling density. This will need to be explained. We attribute this phenomenon to the time dependence of structure rearrangements. The StL amplitude increases much faster at low sampling density and thus allows less time for the growth of new structural states. Consequently, a low sampling density gives the appearance of an extended LV region.
Figure 2.2: SAOS stress sweeps at varying sampling densities plotted with a variety of material functions using linear scaling. Figure 2.2a shows the storage and loss moduli and Figure 2.2b the complex and tangent function. Each LV function provides a nice LV baseline in the low stress regime, followed by classic shear thinning behavior, which is observed as the sample leaves its LV regime. The onset of non-linearity occurs at smaller stress/strain when probing with high sampling density.

The deviations from linearity are gradual. This makes it difficult to assign a meaningful stress or strain limiting value for the onset of non-linearity. To explore this question in detail, we apply a continuous and a discrete method to determine how best to describe the onset. In addition, two LV material functions were studied which address a key question, as to whether an additive function, $G^* (=\sqrt{G'^2 + G''^2})$, or a multiplicative function, $\tan\delta$, is more appropriate and sensitive to predicting non-linearity. For the following analysis, we selected both, $G^*$ and $\tan\delta$. Regardless of whether the storage or loss modulus deviates first, the deviation will be captured by both functions since they depend on both storage and loss modulus, but in different ways.

In our first approach, we express $G^*$ and $1/\tan\delta$ with a non-linear continuous empirical fitting function and the gradient of that function

$$y = \frac{y_b}{(1 + (Bx)^a)^{b/a}}$$

$$\frac{\partial \log y}{\partial \log x} = \frac{-b(Bx)^a}{(1 + (Bx)^a)}$$

(3)
in which \( y \) represents \( G^* \) and \( 1/\tan \delta \), respectively, and \( x \) was set equal to \( \sigma_a \) and \( \gamma_a \). The form of this function was inspired by Carreau-Yasuda model (Yasuda et al. 1981). To preserve the general shape for all material functions (downturn due to yielding), we opted to fit \( 1/\tan \delta \) rather than \( \tan \delta \). The LV baseline values are captured in the \( y_b \) parameter. Fitting parameters, \( a, b, B, y_b \), were optimized with the IRIS software (Winter 2006). An onset criterion was chosen to be a 5% deviation from the LV baseline, \( y = 0.95 y_b \). The log-log gradient of the fit function, \( \delta \log y / \delta \log x \), served as a second criterion. A value of 0.05 in the log-log scale was chosen to identify the onset stress and strain. Figs. 3a,b show the calculated stress and strain values from these criteria. As the sampling density increased, the onset stress and strain decreased for both \( G^* \) and \( \tan \delta \) with this criterion. The variation in onset values is much more extreme in the case of \( \tan \delta \) than in \( G^* \). Generally, the values from both gradients give lower critical onset values. The onset stress values ranged from 99.6-542 Pa and strains from 0.42-3.2%.

![Figure 2.3: The onset stress and strain amplitudes calculated from \( y(x) \) and the gradients (eq. 3) based on data from Figure 2.2. Both \( G^* \) and \( \tan \delta \) fit functions and their gradient were used. As sampling interval increased, the onset stress/strain decreased, which indicates the importance of exposure time at increased stress/strain as will be discussed below.](image)
Instead of using an analytical fit function, eq. 3, the data from Figure 2.2 can also be analyzed in their original digital format. Such discrete analysis is easier to perform. For a given material function, a baseline was established by averaging discrete data points in the linear portion of the SAOS stress sweeps. The onset of non-linearity was found, by our definition here, when the sample deviated from its baseline by 5%. The two data points before and after the deviations, \((\gamma_1, \sigma_1)\) and \((\gamma_2, \sigma_2)\), defined the region of non-linear onset, meaning that the onset of non-linearity occurred at some value in between these two points. A meaningful value for the onset stress was found by linear interpolation between \(\sigma_1\) and \(\sigma_2\). The interpolated value at which a 5% deviation occurred was chosen as onset stress, \(\sigma_c\). The same procedure was repeated for the onset strain.

A discretized log-log gradient was defined as

\[
\frac{\partial \log(y)}{\partial \log(\sigma)} = \frac{\log \gamma_{n+1} - \log \gamma_n}{\log \sigma_{n+1} - \log \sigma_n} .
\]  

(4)

Wherever the gradient value exceeded 0.05, two neighboring data points were identified and the above averaging method was repeated to find the onset stress/strain. The resulting values from this method are shown in Figure 2.4. All onset stresses/strains from the discrete method fluctuate only slightly with respect to sampling density. All onset stresses from this method were found to be between 77-177 Pa and with strains from 0.43-1.24%. These values are quite low when compared to values from equation fitting. While it is not as clear as in the case of continuous fitting method, \(G^*\) again appears to express lower onset values than \(\tan \delta\). This leads us to the conclusion that perhaps \(G^*\), an additive type function, is more appropriate when defining the onset of non-linearity than \(\tan \delta\), a multiplicative function. Furthermore, the gradient method once again assigns lower onset values for the crucial stress and strain.
When comparing the onset stress/strain values from this analysis, it appears that both the fitting function and the discrete method predict similar values for high sampling density. However, the fitting function predicts higher onset stresses/strains at low sampling densities meaning great care must be taken when defining experimental parameters. For the remainder of this study the gradient of the discrete baseline method will be used to identify the onset of non-linearity. This method suggests low onset values, which appear to be independent of sampling density. Ten samples per decade will be used for the remainder of the study.

2.3.3 Yielding Determined by SAOS-LAOS-SAOS (SDS)

A key feature of the CTPB/clay composite is that once yielded under sufficient stress or strain, it is unable to recover its virgin structure. It undergoes an irreversible structural transition, of which we take advantage in the following way. Each experiment starts with a virgin sample. We periodically expose the sample to brief periods of LAOS. Before and after each LAOS application, the sample is characterized with SAOS for LV characterization. In this way, we systematically characterize the effect of the deformation
using simple linear viscosity. A similar characterization has been used in previous studies
in which structural characterization was performed with optical microscopy rather than
SAOS (Hu 1998, Franceschini 2014). Strain amplitude and duration of the applied
deformation are the two user defined parameters in such an SDS experiment, see Figure
2.5. Such a method is not limited to LAOS deformations and in fact other potential
deformation mechanism were briefly investigated here. In our first experiments, SDS were
repeated multiple times while changing strain amplitude and maintaining constant
deformation times. In the second experiment, we varied the LAOS duration while
maintaining a constant strain amplitude. Both, increasing strain amplitude and increasing
LAOS time lead to irreversible structural changes once a critical stress or strain amplitude
is exceeded and the sample yields, i.e. causes permanent deformation. A final setoff
experiments was performed using a steady-shear rate as a deformation by applying a
constant shear rate to the sample for some period of time.

Figure 2.5: Timing of the StL (Figure 2.5a) and SAOS-Deformation-SAOS
(SDS) method (Figure 2.5b) in which large stress/strain amplitudes are used to
alter the sample’s structure and SAOS to rheologically probe the evolving
structure. The LAOS amplitude is increased in a stepwise fashion (left) or the
Deformation exposure time is increased in additive fashion (right).
Thirteen SDS cycles with incrementally increasing strain amplitudes (during the LAOS step) were performed at room temperature. Each deformation cycle lasted 30 min and was carried out at 1 rad/s. Initially the applied strain was kept below sample’s onset strain ($\gamma_A < \gamma_c$) as learned from the StL transition behavior. The increasing strain amplitudes eventually exceed the critical strain ($\gamma_A > \gamma_c$). Frequency sweeps were applied after each LAOS period. At low strain amplitudes, only small deviations are seen (highlighted further in the Figure inserts) while larger strain amplitudes become effective in lowering the moduli and thereby indicating a loss in connectivity as demonstrated in Booij-Palmen (Figure 2.6a) and Winter plots (Figure 2.6b) (Booij 1982, Winter 2009). Both plots effectively highlight deviations from the virgin sample. The Booij-Palmen plot (Booij 1982) indicates that a traditional horizontal shift does not superimpose the shear modified composite. An additional vertical shift is needed as will be shown below. The Winter plot (Winter 2009) highlights the connectivity reduction in CTPB/clay while maintaining its solid properties when probed in SAOS, marked by a vertical line in the low modulus portion of the data.

Figure 2.6: SAOS frequency sweeps after LAOS applications at stepwise increasing amplitude, expressed in a Booij-Palmen (Figure 2.6a) and Winter plot (Figure 2.6b). LAOS was applied for 30 min each at $\omega=1$ rad/s. Only selected SAOS data are shown.
To further highlight the deviations from the virgin sample, the SAOS moduli after each LAOS application were subtracted from the initial moduli of the virgin sample. The storage (Figure 2.7a) and loss modulus (Figure 2.7b), after the subtraction, begin to deviate mostly at high frequencies. Deviations eventually extend out to the low frequency regime as the strain amplitude was further increased. The first strain at which a deviation was observed at all frequencies is 0.75%. For the purpose of this study, we will say the deviation occurred somewhere between 0.5-0.75%. This value agrees well with the values calculated from the gradient of discrete baseline in the previous section, indicating that the onset of non-linearity corresponds to beginning of yield.

Figure 2.7: Storage (Figure 2.7a) and loss moduli (Figure 2.7b) subtracted from the virgin sample’s baseline. Data taken from Figure 2.6.

2.3.4 Time Dependence of Structural Change During Yielding

Yielding involves flow and flow needs time. The duration of exposure to LAOS turned out to be an important parameter. The gradual change due to LAOS was monitored by exposing a fresh sample to 45 SDS cycles at a constant LAOS strain amplitude of $\gamma_a=0.1$ for 2 min at 1 rad/s per cycle. Each LAOS cycle consisted of approximately 35 oscillatory rotations. A strain amplitude was chosen well above the sample’s yield strain to ensure
rapid structure evolution. Since the sample is unable to recover we can treat each LAOS time as additive. As the duration of LAOS time increased, LV properties changed significantly, see Figure 2.8. The dynamic moduli decreased, and the characteristic relaxation times increased. Eventually at long deformation times, it appears that the sample’s LV properties approaches a steady-state, indicating no further softening/modulus reduction was occurring.

Figure 2.8: SAOS frequency sweeps after various LAOS times in modulus and tanδ (Figure 2.8a), Booij-Palmen (Figure 2.8b) and Winter plot (Figure 2.8c). The LAOS strain amplitude was γ_a=0.1 and the LAOS frequency was 1 rad/s for 2 minutes.

The LAOS shearing time per cycle was kept constant (2 mins) meaning the overall LAOS time increased (see Figure 2.5b). After each shearing period, SAOS data was
measured and then shifted using deformation time-time superposition with the virgin sample as reference. Surprisingly, the moduli superimposed (Figure 2.9a) very nicely on top of each other. The modulus reduction was expected to happen, but the fact that it does so in a self-consistent manner is surprising. To successfully superimpose, both horizontal, $a_2$, and vertical, $b_2$, shifting was needed. If only horizontal shifting were needed, Booij-Palmen curves would have overlapped. When shifting the moduli of the sheared sample onto the moduli of the virgin sample, we need to shift upwards (higher modulus) and to higher frequencies. The corresponding shift factors are plotted in Figure 2.9b Initially a large shift is observed indicating a fast softening of the modulus. However even after 90 minutes of exposure to the LAOS deformation, the shift factors are still changing slightly, meaning a steady-state has not been reached. This further indicates the importance of time evolution associated with yielding. This is similar to the effects of Miner’s Law to describe fatigue as being an additive type process, where prior deformations play a role in the material’s overall failure.

Figure 2.9: Master curve after using LAOS time-time shifting (Figure 2.9a) and the corresponding shift factors (Figure 2.9b).
2.3.5 Time Evolution of Structural Changes during Steady Shear Yielding

As previously mentioned, the deformation step is not limited to LAOS deformation. We have also briefly explored the ability to use steady-shear to deform the sample. Two separate virgin samples were formed in the rheometer and then exposed to shear rates of 0.005 and 0.0075 s\(^{-1}\) for 60 seconds for 15 cycles with SAOS frequency sweeps performed between each cycle. This results in a strain of 30% and 45% per step which is well-above the yield strain. This was followed by 1-hour deformations at the same shear rate for 5 additional cycles. This softened the sample further to the point where it was independent of deformation time. Select SAOS frequency sweeps are shown after various in Figure 2.10, defined by the total amount of strain input into the sample. Figure 2.10a,b correspond to the storage modulus (a) and Winter plot (b) of the samples exposed to a shear rate of 0.005s\(^{-1}\) shear rate and Figure 2.10c,d to the a shear rate of 0.0075s\(^{-1}\). The “saturation” value in these curves is the point at which the SAOS frequency sweeps are independent of deformation time. Again here, the deformation is considered additive and is reported as a function of total strain deformation.
Figure 2.10: SAOS frequency sweeps after various amounts of yielding when performed to a shear rate of 0.005 s\(^{-1}\) with the storage modulus (Figure 2.10a) Winter plot (Figure 2.10b). A saturation after long times was observed and is called the saturation time. With the same plots in with a shear rate of 0.0075 s\(^{-1}\) for the storage modulus (Figure 2.10c) and Winter plot (Figure 2.10d)

At long deformation times, SAOS frequency sweeps were found to be independent of time, “saturation time”. This is to say as much deformation as possible had occurred under these specific deformation conditions. A key question that remains is to determine whether this saturation value depends upon the shear rate. The sample’s saturated storage and loss modulus are shown in Figure 2.11. The Winter plot reveals that the sample exposed to a higher shear rate (0.0075 s\(^{-1}\)) was softer than that of the lower shear rate (0.005 s\(^{-1}\)). Reasons for this will be addressed in the discussion portion of this chapter but clearly there is a
shear-rate dependence in the final state of the composite, along with the fact that it takes time to reach that final steady-state.

Figure 2.11: Winter plot after both composite’s become independent of deformation at a shear rate (marked).

2.3.5 Effect of Frequency on Non-Linearity and Yielding

Up to here, all StL amplitude sweeps were shown for a single frequency (1 rad/s). However, frequency is an important parameter. StL measurements at 4 different frequencies of 0.42, 1, 4.2 and 10 rad/s showed that varying frequency strongly affects a sample’s LV properties. Storage and loss modulus both increase with frequency (Figure 2.12). The LV baseline trends look pretty much the same for both strain (Figure 2.12a) and stress (Figure 2.12b).

Figure 2.12: StL stress sweeps at varying frequencies versus strain (Figure 2.12a) and stress (Figure 2.12b) amplitudes.
The sensitivity to large stress or strain becomes more obvious when normalizing the complex moduli with respect to their respective LV baseline (Figure 2.13 a,b). This removes the vertical modulus shift due to frequency, which is not the focus of this experiment. In this way, the onset of non-linearity can be compared for the different frequencies. Figure 2.11a shows the data set as a function of strain and Figure 2.13b as a function of stress. For our samples, Figure 2.13b demonstrates that normalized complex modulus deviate from the LV baseline much ‘earlier’ at low frequencies than at higher frequencies. The samples seem to have a lower yield stress when measuring at low frequencies. This completely changes when plotting the same data against strain (Figure 2.13a): the onset of non-linearity becomes independent of frequency. All curves collapse onto a single curve with a single onset value for the strain! This suggests that, for the CTPB/clay system, yielding should be thought of as a strain activated process instead of stress activated.

Figure 2.13: Complex moduli of Figure 2.12 normalized with respect to their LV baseline value, plotted against strain (Figure 2.13a) and stress (Figure 2.13b) amplitude, respectively. The yield/onset stresses and strains were calculated using the gradient of the discrete baseline method.
The resulting yield stresses were plotted as a function of frequency. Since yield strains were independent of frequency, they are not shown. A simple power law dependence was used to establish a relationship between yield stress and frequency in Figure 2.14.

\[
\sigma_y = A\left(\frac{\omega}{\omega_0}\right)^b
\]  

(5)

A,b are fitting parameters and \(\omega_0\) is an arbitrary reference frequency. It remains unclear how the fitting parameters are related to the sample’s intrinsic properties.

A similar qualitative trend between yield stress/strain relationship was observed when performing StL measurements at different temperatures (5, 25, and 50ºC) at a constant frequency (Figure 2.15). Figure 15a,b shows the StL behavior plotted at 3 different temperatures with the lowest temperature having the highest LV baseline. When normalized by their LV baseline, once again the strains collapsed onto a single curve, the stresses didn’t (Figure 2.15c,d). This is to say the yield strain was independent of temperature and the yield stress increased at lower temperatures.
2.4 Discussion

The CTPB/clay composite proved to be an ideal material system to study the onset of non-linearity and yielding in a systematic fashion. Not only is the material a solid with a distinct yield condition, once yielded, it is unable to recover its virgin structure. Furthermore, the sample’s ability to form its structure after (and not before!) having been loaded into the rheometer, in between cone and plate fixtures, guarantees a well-defined initial state for all experiments. It is a stress-free solid (physical gel), which then gets deformed uniformly, unlike in a parallel plate geometry or the vane tool. Small amplitude oscillatory shear (SAOS) serves to determine the evolving structural states of the sample.
or more precisely, the rheological consequences of the structural changes which get induced by large amplitude oscillatory shear (LAOS). To determine the morphological structural changes associated with yielding the composite would require additional characterization, which is outside the scope of this rheological study. However, previous studies have shown intercalated clay aligns in the direction of shear and result in a loss of mechanical properties (Giannelis 1999, Krishnamoorti 2001, Schmidt 2000). We speculate a similar process is occurring here.

Two different experimental protocols (StL and SDS) deliver complementary results about the onset of non-linearity and yielding. The StL experiment applies oscillatory shear at larger stress amplitudes and causes a transition from SAOS to LAOS. Single frequency StL stress ramps show the onset of non-linearity and its frequency/temperature dependence. The SDS experimental protocol alternated between SAOS, deformation, and back to SAOS, and repeated this sequence many times SDS provides an experimental method to decouple yielding behavior from non-linearity deviations by separating the deformation and characterization steps. This was made possible by the fact that the material did not recover. For our sample, both onset of non-linearity and yielding occurred at about the same strain amplitude between 0.5-0.75%. In this way, either StL or SDS can be used to detect the onset of yielding.

Repeated StL stress ramps at different frequencies, each with a new sample, indicate that the CTPB/clay composite’s yielding behavior is a strain activated process, not stress activated (Figure 2.10). The onset of non-linearity, which for our sample appears to be synonymous with yielding, moves to higher stresses when shearing at higher frequencies. A power-law relates yield stress and frequency in the small range of frequencies tested
(0.42-10 rad/s). In comparison, the sample’s yield strain did not change with frequency or temperature. The same trend (strain activated) held for StL at increased temperature. As the temperature was increased, the yield stress decreased while the yield strain stayed constant. The temperature/frequency stress dependence is self-consistent in that to hit a target strain, a lower stress amplitude is needed for softer samples.

In both the StL and SDS experiments, deformation time of LAOS exposure played a key role. The experiments are very different but the message is consistent. The exposure time was increased in StL experiments when increasing the sampling density and in SDS experiments when staying longer in LAOS mode. In StL experiments, a high sampling density resulted in additional time spent at intermediate stresses/strains. The sample’s structure was given time to adjust and thus the modulus began dropping off at a lower stress amplitude. However, such an experiment does not provide sufficient time to reach a steady state due to the imposed stress/strain. To get closer to a steady state, SDS measurements at a constant strain amplitude above the yield strain were carried out. SAOS data for larger and larger LAOS exposure times show the approach of a steady state (Figure 2.9). Despite applying LAOS for a total of 90 minutes, the composite structure is still rearranging as expressed in the LV data.

A solid near its gel point is characterized by a low modulus and long relaxation times (Figure 2.16) (Momani 2016). These are the characteristics of the CTPB/clay composite. Our virgin sample is a soft solid well above its gel point. Exposure to various LAOS times caused the sample to undergo a solid to solid transition near (remaining above the gel point). The internal connectivity (bond probability) reduces with LAOS time. SAOS frequency sweeps superimpose but require a time shift as well as a modulus shift. Similar
behavior has been seen in epoxies at varied extent of reaction (Adolf 1990) and coacervates through variations in salt concentration (Liu 2016). Such studies suggest a universality of soft solids above their gel point, independent of the mechanism used to reduce their bond probability (deformation, stoichiometry, and salt concentration). In all three classes of materials, both horizontal and vertical shifting is needed to impose the data. Such an understanding is not yet understood.

![Diagram showing characteristic LV properties of soft solids above their gel point connectivity](image)

Figure 2.16: Characteristic LV properties of soft solids above their gel point connectivity, $p_c$. $p_c$ marks the percolation threshold. With increasing bond probability beyond the gel point, the characteristic material times decay and the characteristic modulus increases (Vilgis 1998). This behavior has also been found during the exfoliation of the CTPB/clay (Momani 2016). In this study, the “virgin” sample is close to its equilibrium state (marked with a thick vertical line). LAOS shear modification moves the soft solid closer to its physical gel point. As a consequence, its modulus decreases and its characteristic times get longer after having been exposed to more and more LAOS (longer deformation times). The magnitude of the shift is shown in Figure 2.9b.

The sample is a solid before and after having been exposed to the deformation steps. Yielding produces a solid to solid transition. Orientation of intercalated clay sheets has
been previously reported (Giannelis 1999, Krishnamoorti 2001, Schmidt 2000). We speculate that in the composite, the exfoliated clay sheets orient under the imposed shear and the oriented sheets are separated within the polymer matrix. The reduced particle-particle interaction and reduced direct connectivity between particles leads to the lowering of the modulus as seen in the SAOS data. The orientation is expected to develop gradually and should occur at local length scales first, which might be the reason that the orientation effect shows up first in the high frequency data. As the sample is subjected to higher strain and at longer times, more and more clay sheets are expected to orient on a global length scale. As this occurs, shear effects become noticeable at lower frequencies (Figure 2.7). The effect of sheet alignment should saturate eventually, and LV material functions would become independent of further shearing. As discussed above, long times are required to reach such steady state.

2.5 Conclusions

The CTPB/clay composite is a soft solid, which permanently reduces its internal connectivity upon yielding and, hence, is an ideal model system for the study of yielding. Large stress/strain amplitudes result in an irreversible solid to solid transition. When comparing the onset of non-linearity in a traditional SAOS to LAOS (StL) stress growth experiment with yielding in a SAOS-LAOS-SAOS (SDS) experiment, about the same onset values were found. For our CTPB/clay composite, the onset of non-linearity occurred at about the same strain amplitude as yielding. This yield strain was found to be independent of both frequency and temperature. However, the yield stress increased when increasing the frequency and/or lowering the temperature. An additive function, $G^*$, was most sensitive to indicate the onset of non-linearity when comparing to other LV material
functions. Yielding allows flow and naturally introduces a time dependence, which became apparent in StL when increasing the stress amplitude more slowly (using higher sampling density) and in SDS when increasing the LAOS time. The finite rate of yielding must be accounted for in experimental planning. When the stress/strain amplitude in StL is raised too quickly, for instance, the LV region appears to be larger than it actually is.
CHAPTER 3
EFFECT OF PLATLET SIZE IN A SOFT SOLID NANOCOMPOSITE:
PHYSICAL GELATION AND YIELDING

3.1 Introduction

Particle filled polymer composites take advantage of the reinforcement which non-Brownian fillers provide when dispersed in a soft polymer matrix. In addition to particle loading, particle/polymer interactions and particle/particle interactions, geometrical parameters of the filler govern the composite’s performance including its shape, size, and orientation. A standard grouping of particle effects is based on shape 1D (rods/fibers), 2D (platelets) or 3D (spheres) (Kalfrus 2007, Schadler 2007). Best understood among asymmetric particles are the effects of 1D fillers (fibers) in a composite. In a recent review, Pickering and co-workers, highlighted the need for oriented, high aspect ratio fibers to maximize the composite’s final modulus under tension and compression (Pickering 2016). When fibers are aligned in the direction of uniaxial stress, both the fibers and the matrix material help withstand the stress and the material’s modulus is increased. However, eventually this effect begins to saturate at higher degrees of orientation and/or increasing fiber length, and thus there is limited further increase in modulus from perfectly aligned and slightly offset fiber orientation (Tian 2014). When the matrix polymer is a liquid, the 1D fillers have been shown to induce a liquid to solid transition due to the 1D fillers connecting to form a sample spanning structure. Studies on carbon nanotubes of varying lengths in different polymer matrices have shown the percolation threshold is shifted to lower loadings as the aspect ratio of the fiber increases (Cipiriano 2007, Wu 2010). Finally, shear induced orientation
of the nanotubes was found to reduce the network’s connectivity to the point at which the composite reverts to a liquid, as determined by the composite’s storage modulus (under shear) (Alig 2008). Although it does not revert to the initial state of the neat polymer, because some connectivity from the filler is still realized.

The rheological effects of 2D fillers in a polymer matrix are far less explored. This may be due to difficulties associated with achieving and characterizing single sheet platelets. To our knowledge, only four experimental studies have explored the reinforcing effect platelet size has on a polymer composite’s final properties (Boo 2007, Sun 2009, Weon 2005, Mitchell 2002). Weon and co-workers used clay, like the one in the present study, while other studies used synthetic 2D materials such as zirconium phosphate. In their study, they extruded nylon 6/clay composites and altered the clay’s platelet size and orientation by varying the extrusion conditions. Specifically, equal channel angular extrusion was used which allowed for applying different shear forces on the particle (Segal 1995). After fabricating a series of different composites, the mechanical properties were measured and found both orientation and platelet size affected the composites properties. However, these results effects (both rheological and tensile) were somewhat overshadowed due to the high viscosity/modulus of the neat nylon matrix. It became clear that a softer polymer matrix is preferable for our study to amplify the effect of fillers.

The polybutadiene/clay composite proved to be a model system to study the effect of platelet size and orientation on the rheological affects of the filler. Specifically, we took advantage of the fact that exfoliation could be achieved using a PB/CTPB (or HTPB) blend but not PB/clay alone. Specifically, we reduce the clay’s platelet size and oriented the clay sheets using two very different forms of flow treatment before and after exfoliation. The
first was a chaotic flow treatment of the PB/clay suspension to reduce the size of the clay particles, which was followed by the exfoliation (Liu 2015). A second flow treatment was performed in the rheometer which oriented the exfoliated clay sheets in the polymer matrix. Shear yielding shifted the composite’s LV properties by lowering the modulus and increasing relaxation times (in the case of soft solids). The combination of size reduction and yielding, caused the sample to permanently soften and transition into a liquid. Size reduction or yielding alone was not enough to induce a transition into the liquid state.

### 3.2 Experimental

#### 3.2.1 Sample Preparation

A key point of this work was to have particle size reduction occur first followed by clay exfoliation. This avoids competition between size reduction and physical gelation (exfoliation). Clay exfoliation was postponed by embedding the particles in the non-functionalized polybutadiene (PB) which is known to prevent particle aggregation but has no effect otherwise (Chen 2005). In this way, clay particles were merely suspended in a liquid PB matrix. The PB/clay suspension is in the liquid state as needed for an effective particle size reduction in the planetary mixer, which relies on flow at extensive stress.

Specific steps are as follows: 84 wt% PB and 16 wt% clay were massed and homogenized in a planetary mixer at 3000 RPM for 1 minute. The mixture turned opaque due to the clay being suspended in the liquid PB matrix. Samples were then subjected to chaotic flow treatment in the mixer by adding four cylindrical ceramic pebbles into the mixing cup. A rotational speed of 3000 rpm was used in 2 min cycles with a 1 min cooling period in between each step. For increased levels of size reduction, the amount of high shear treatment was increased to as much as 20 minutes. The exfoliation was then initiated
by adding CTPB into the system. This reduced the clay loading from 16wt% to 8wt% with respect to the total polymer (50/50 mixture of PB and CTPB). Immediately after gently mixing the CTPB into the PB/clay suspension (3000 RPM for 1 minute without the mixing pebbles), samples were loaded into the rheometer, which was then set to the prescribed gap height of the cone-plate geometry. It is essential to place the sample between the rheometer fixtures before structure formation can occur. This avoids the sample’s structure being altered during sample loading (Tanna 2017). Exfoliation was then carried out by annealing the sample at 80°C for 10 hours and formed the physical gel. The above prescribed method presents a standardized way to generate stress-free physical gels (denoted as “virgin” samples), which are unaffected by the mixing and/or by the sample loading into the rheometer. This established a reproducible starting condition for LV characterization. An alternative method to create a well-defined structure would be by applying large shear after loading the exfoliated sample into the rheometer. We employ both methods while noting that the two sample states are vastly different in their rheology (random versus aligned clay particles). We also noted that sample are poorly reproducible when exfoliating before loading into the rheometer but not shearing afterwards.

3.2.2 Chaotic Flow Treatment in Planetary Mixer

Intense stressing and mixing was achieved by adding four cylindrical ceramic pebbles (h =10.0mm, r= 4.80mm) into the mixing cup with the PB/clay suspension. The presence of the pebbles changed the sample’s flow profile. The sample divides when flowing around a pebble and recombines again behind the pebble. During the division, the suspension gets subjected to large shear forces, which caused clay particles to reduce their size. In addition to the large shear forces, size reduction was attributed to both particle-particle and particle-
pebble collisions. In the upcoming sections, clay subjected to this treatment will be referred to as “size reduced samples”.

### 3.2.3 Instrumentation

Rheological measurements were performed on a stress-controlled Stresstech ATS with 25-mm cone and plate (or 25-mm parallel plate) fixtures. Yielding was performed at a shear rate of 5s\(^{-1}\) for 180s (\(\tau=900\)) followed by a second SAOS characterization. After yielding, creep recovery experiments were performed by applying a stress of 1Pa for 2.5 hours and then releasing the stress and monitoring the strain behavior for an additional 2.5 hours.

Clay particle size distributions were measured in a FEI Magellan Field emission scanning electron microscope (SEM). The oMMT particles had been separated from the polymer for improved contrast. For this purpose, PB/clay was dissolved in THF and clay particles were allowed to settle to the bottom of the vial. The supernatant, containing polymer and THF, was removed and the washing process was repeated until the majority of the polymer had been removed. Although the supernatant appeared clear, some small clay particles may have been lost during washing. These exceedingly small particles are not the focus of this study as their rheological effect would be minimal compared to that of the larger platelets.

The sediment was diluted with THF to appropriate concentrations, spin coated on a silicon wafer, gold sputtered, and imaged via SEM. This allowed us to determine the size distribution of clay platelets. Such an analysis assumes that the clay particle’s aspect ratios were large enough to cause them to lay flat, not standing, on the silicon wafer after having been spin coated. This provides the platelet lateral dimensions.
3.3 Experimental Results

3.3.1 Rheological Response of Polymer and Composite before Size Reduction

The neat PB, CTPB, and their 50/50 blend (no clay) exhibit the typical LV features of a liquid polymer (Figure 3.1a). This is not surprising because both polymers are low molecular weight and the measurements were performed well above their glass transition temperature. The CTPB, PB and its 50/50 blend have almost identical LV properties. This indicates that PB and CTPB are miscible and that the materials overall rheological response is unaffected by the dilution of functional end-groups when mixing the CTPB into PB in a 50/50 blend, as expected.

Addition of clay (no size reduction yet) drastically changes the LV properties. Eight weight percent clay was added to PB, CTPB, and the 50/50 blend; their LV properties are compared in Figure 3.1b. As described in the sample preparation section, the polymer/clay samples were mixed and quickly transferred into the rheometer before exfoliation could take place (only needed for CTPB or PB/CTPB matrices) and then annealed in the rheometer. The procedure resulted in the formation of a stress-free structure, which quickly transitioned to form a soft solid in the rheometer (physical gel due to clay exfoliation). The solid state is indicated by the appearance of a plateau in the storage modulus, $G'$, at low frequencies (Figure 3.1b). In terms of connectivity, differences between CTPB/clay and the blend/clay are minimal (Figure 3.1b). This highlights the importance of having the carboxyl functionality to form the physical gel.

The rheological behavior is fundamentally different when using PB instead of CTPB as the matrix material. Without the functional end-groups, the PB/clay mixture remains in a liquid state. It is a suspension of clay particles in a viscoelastic liquid as
needed for size reduction flow in the planetary mixer. These findings were key in designing our size reduction procedure.

Figure 3.1: SAOS master curves of neat polymers (and blend) (Figure 3.1a) and their composites (Figure 3.1b) after adding eight weight percent clay. The clay composites containing CTPB were exfoliated in the rheometer to avoid any shearing during sample loading (“virgin samples”). Composites containing CTPB with its functional end-group form a soft solid as indicated by the low frequency plateau in $G'$. 

3.3.2 Particle Size Reduction

The PB/clay suspension was subjected to intense chaotic flow treatment as discussed above for varying amounts of time. In this state, PB is simply acting as a carrier for the clay particles (no gelation occurred) and as a stress transfer medium. The chaotic flow treatment breaks aggregates into individual clay particles and, also reduces the individual particle’s lateral size. Furthermore, the flow treatment may also reduce the number of platelets per clay stack and even may cause partial exfoliation of clay. Figure 3.2 compares the x-ray scattering profiles of the PB/clay suspension before and after 20 minutes of chaotic flow treatment. In this case, the extent of exfoliation caused by the chaotic flow is minimal as indicated by the minimal reduction in peak intensity. Figure 3.3 compares the particle’s lateral size distribution after 0 (left), 10 (middle) and 20
(right) minutes of flow treatment based on measuring the projected 2D surface area of the particles on a spin coated substrate. The imaged area of the original clay particles (non-reduced; polymer removed) was found to be 0.75 µm\(^2\) as compared to 0.51 µm\(^2\) and 0.45 µm\(^2\) after 10 minutes or 20 minutes of flow treatment, respectively. Size reduction clearly can be seen in both the SEM images and the size distribution profiles. The most significant change in the platelet size distribution was in the large platelets i.e. larger platelets being made much smaller. This is reflected in the histograms by disappearance in the tail end of the distributions. Large particles occupy more space and, thus, the probability of having a platelet cut by the grinding or collisions is increased. At these specific flow conditions, the effect of chaotic flow begins to saturate at increased treatment time. The 10 to 20 minutes size distribution profiles differ only slightly. This further indicates that flow treatment is most effective while large particles are present.

**Figure 3.2:** Scattering profiles of samples measured before and after 20 minutes of flow treatment. This indicates that the flow treatment did not significantly exfoliate the clay particles.
3.3.3 Effect of Size Reduction on Rheology

SAOS master curves of the virgin stress-free nanocomposites with size reduced clay (Figure 3.4a, yellow triangles) are slightly lower than those of large non-reduced clay (Figure 3.4a, blue circles). The difference between the two samples is noticeable but not very pronounced. Both still form soft solid physical gels where the size reduced had a slightly lower plateau modulus and increased relaxation times thereby, indicating size reduction caused a slight decrease in connectivity. The master curve of the virgin size reduced composite could be shifted on top of the non-reduced sample through a second (free) shift. An acceptable superposition was observed with a slight deviation in tanδ at high frequencies. Size reduction caused an increase in the relaxation time (horizontal shift factor 1.05) and a modulus reduction (vertical shift factor 0.70). Relaxation times are difficult to assign for solids, linear liquid homopolymers are much easier (Friedrich 2008). While the “second shift” is not perfect, it helps to assign meaningful relaxation times to quantitively describe the effect of size reduction in the virgin samples.
Figure 3.4: SAOS master curves of the virgin (Figure 4a) and the yielded (Figure 4b) composite with non-reduced and size reduced sample. Virgin and yielded sample data are also plotted for non-reduced (Figure 4c) and size reduced (Figure 4d) composites. The combination of size reduction and yielding induced a solid to liquid transition. Either yielding or size reduction by themselves caused a softening in the solid.

The exfoliated virgin samples were then yielded by shear, which is known to irrecoverably soften the composites structure through a reverse gelation type process (Tanna 2017). Such yielding was invoked by shearing the sample at a shear rate of $5\text{s}^{-1}$ for 180s between cone and plate fixtures to create a uniform strain throughout the sample. The same uniform shear treatment was chosen for all samples. Afterwards, the samples were subjected to SAOS for LV characterization. Without size reduction, yielding reduced the SAOS modulus, but the sample clearly remained a solid (Figure 3.4b, green, triangles). In the case of the reduced platelet size, a much larger loss in connectivity occurred: the yielded
sample is no longer a solid i.e. yielding after size reduction induced a solid to liquid transition (Figure 3.4b, red, squares). This was marked by the downward slopping nature of the storage modulus. To further highlight the effect of yielding, the virgin and yielded samples for the non-reduced (Figure 3.4c) and size reduced clay (Figure 3.4d) are plotted against each other. The moduli of the yielded non-reduced clay containing samples were superimposed onto the corresponding virgin sample. Yielding caused a substantial shift in both characteristic times and characteristic moduli, particularly at low frequency and was much more significant than the size reduction. A much larger horizontal time shift of 2.0 and a modulus shift of 0.30 were needed for the superposition, relative to the size reduced virgin sample (without yielding). This indicates that the yielding plays a key role in the softening process, especially for the size reduced composites. Obviously, the dynamic moduli of the liquid and solid samples do not superimpose due to their inherent differences in the low frequency regime.

3.3.4 Effect of Varying Platelet Size + Yielding

So far, we compared the LV properties of composites with the most severely size-reduced clay (20 minutes of flow treatment) to that with non-reduced clay. Intermediate states of size reduction (varying the amount of flow treatment) show the gradually changes in the composites rheological response. SAOS measurements were carried out with a parallel plate geometry for ease of the experiment. The parallel plate geometry, as compared to the cone-and-plate geometry, no longer provides a uniform strain, however, the viscoelastic differences between the two are negligibly small in this context and have been experimentally verified. The storage modulus, loss modulus, normalized storage modulus and normalized loss modulus from the SAOS characterization are shown (after
yielding) in Figure 3.5a-d at varying degrees of size reduction, via increased treatment time of PB/clay suspension, in the pebble-stacked planetary mixer. The data sets can be divided into two regimes, marked by the dashed lines in Figure 3.5. In the low frequency regime, there is a heavy dependence on shear treatment (yielding + size reduction). However, at higher frequencies, all the samples converge and become almost independent of shear treatment. The divergence of these curves in the low frequency regime indicate a loss in connectivity due to stronger and stronger size reduction. However, at high frequencies the dynamic moduli converge and become independent of the amount of flow treatment. Potential reasons for this will be explored in the discussion.

**Figure 3.5:** SAOS master curves after various amount of size reduction and yielding (5s\(^{-1}\) for 180s) storage modulus (Figure 3.5a) loss modulus (Figure 3.5b) normalized storage modulus (Figure 3.5c) normalized loss modulus(Figure 3.5d). The dashed line in each figure marks the division between a strong dependence (left of the dashed line) and weak platelet size dependence (right of the dashed line).
Further examination of the storage modulus in the low frequency regime suggests the solid to liquid transition occurs when size reduction extends beyond 10 minutes of flow treatment. To further highlight this, a Winter plot was constructed (Figure 3.6a). The disappearance of the straight vertical line, indicating a frequency independent modulus value, highlights that the solid to liquid transition occurs when treating the sample with more than 10 minutes of chaotic flow (Winter 2009). To further confirm this, samples were transferred into glass vials and left at room temperature. After two weeks, an image of the vials was taken (Figure 3.6b). Only the sample exposed to 10 minutes of flow treatment could flow down the vial after two weeks, indicating it was either a liquid (that is unable to hold its shape) or had such a low modulus that it was not able withstand the force from gravity. This type of experiment represents a simplified creep test under elongation flow with the imposed stress being due to gravity. However, the sample may have also had some unquantifiable forces placed on it during unloading from the rheometer. To fully verify the solid to liquid transition, creep and recovery experiments were performed on samples about this critical solid to liquid transition (Figure 3.6c). A shear stress of 1Pa was applied to the shear aligned composites followed by releasing the stress while monitoring the sample’s strain response the entire time. The sample with 3 minutes of treatment showed a full recovery back to its initial state, indicative of a solid, while 10 minutes of treatment never fully recovered indicating it was in fact a liquid. Correlating the SAOS rheology, images of the vials, and creep recovery, provides further proof of the solid to liquid transition. Mild size reduction treatment resulted in a softening of the gel, but the samples remain solids. It should be noted, the sample subjected to 20 min of flow treatment also flowed but an image is not included in Figure 3.6b.
Figure 3.6: Exfoliated clay in the CTPB/PB matrix after size reduction and shear alignment (a) Winter plot (Figure 3.6a), after transfer to a vial and resting for 2 weeks (Figure 3.6b), and exposure to creep at outer diameter with $\sigma = 1\text{Pa}$ for 2h followed by recovery for 2.5h (zero stress) (Figure 3.6c) Samples with mild size reduction (flow treatment < 5 min) are solids while samples with smaller clay platelets (extended flow treatment > 10 min) behave as liquids on the measured time scales.

3.3.5 X-ray

After rheological measurements, x-ray was performed to characterize the microstructure of the composite. The transparent color of each sample along with the disappearance of a MAXS peak indicate that the clay is in fact exfoliated. This agrees with results from Zhu et al., who used a blend of functionalized and non-functionalized PB as matrix polymer and effectively achieved clay exfoliation [16].
3.4 Discussion

The liquid polybutadiene/clay composite proved to be a model system for the study of reinforcing effects caused by 2D filler size and orientation. Rheological effects due to size reduction are most pronounced when combined with orienting the exfoliated clay platelets in the polymer matrix. The platelet size was reduced by intense flow treatment. The effect begins to saturate at 10 to 20 minutes of flow treatment where the difference between the times become small (Figure 3.3 and Figure 3.5 respectively). This is to say that, under our specific operating conditions, the highest possible size reduction (a 40% surface area reduction in clay platelet size) is reached. To further reduce the particle size, more intense forms of shear would have been needed in the planetary mixer or under alternative conditions. It should be noted, experiments were also performed in which clay powder was ball milled and added to the CTPB but the clay aggregated, presumably due to the large surface charges exposed in the clay sheets when exposed to such high shear forces.

The clay particles are highly irregular and asymmetric as mentioned in the introduction. Because of this, the chaotic flow affects the particle’s size and shape on
multiple length scales. This involves breaking up of clay aggregates, reduction in particle lateral dimensions, and breaking apart of stacks into smaller particles including exfoliation. The breaking down of clay aggregates is the first step in the process that occurs and probably requires the least amount of force. This though has little effect on the desired final state of exfoliated sheets in a polymer matrix. Critical to this study is the reduction of the lateral dimensions of clay particles. However, some exfoliation of clay may already occur during the reduction in platelet size in the flow treatment. Previous studies have seen this using electron microscopy and XRD on oMMT (Ramadan 2010). The fact that the SAXS peak mostly remains indicates that our flow treatment is not strong enough to exfoliate the clay in significant ways (Figure 3.2).

Surprising is the narrowing of the peak in Figure 3.2 and the decrease in the average spacing from 2.1 to 1.9nm after flow treatment. We attempt to explain this by the following phenomenon: The polydisperse spacing between clay sheets in a stack broadens the SAXS peak. The largest spacings belong to locations of weakest cohesive force in clay stacks. We assume that this is the location where stacks most likely break under stress from the chaotic flow. The remaining sheets in broken fragments are spaced more narrowly but they are still assembled in stacks. Their average spacing is smaller and more uniform. This results in the shifted and narrowed peak of Figure 3.2. The main exfoliation happens at a later stage of sample preparation after having added CTPB and immediately loaded the sample into the rheometer. Exfoliation occurs over time and causes the modulus to grow substantially as measured in the rheometer. These are the so-called virgin samples.
Upon achieving exfoliated virgin samples of varying platelet sizes, the composite was shear yielded. As previously discussed, yielding caused the modulus to permanently soften (Tanna 2017). We speculate this softening is due to the alignment of clay sheets (Giannelis 1999, Krishnamoorti 2001, Schmidt 2000). Softening due to orientation would agree with findings observed in nanocomposites with 1D fillers in the introduction. The shear sensitivity is largest for the most reduced platelet size, which also requires the smallest strain for effective shear yielding. Vice versa, the original larger platelets create a physical gel which requires a larger shear strain before it yields. Further experimental characterization would be needed to quantify (and confirm) the extent of alignment of clay within polymer but this is beyond the scope of this study.

Both size reduction and yielding cause the modulus to soften and, when used in combination, induced a solid to liquid transition. The key question is to understand the roles platelet size and orientation have on the connectivity of the physical gel. From a gelation point of view, size reduction increased the number of platelets needed to form a sample spanning (percolating) network. This in turn reduces the probability to form physical bonds. We speculate this effect is amplified with yielding because orientated clay sheets require an even larger number of platelets to form a sample spanning percolating network. The connectivity of the gel gets probed at low frequencies which is clearly reduced with decreasing platelet size (Figure 3.5 and 3.6). As the amount of flow treatment was increased, a reduction (and eventually disappearance) in the amount of physical crosslinking was seen. Figure 3.8 shows how this polybutadiene/clay composite maps onto the traditional viscoelastic response of a soft solid above and below its gel point. The initial virgin sample is a soft solid with a well-defined plateau modulus.
corresponding to a discrete value in the figure ($G_e$, $\tau$). Softening occurs and moves the sample closer and closer to its gel point $p_c$ until the solid to liquid transition is induced at which point it is governed by its viscosity, $\eta$. Above the gel point, this is seen by the fairly successful superposition of a size reduced and yielded sample onto the virgin, non-size reduced sample; although slight deviations are seen in $\tan \delta$ (Figure 3.8b). Size reduction partially reverses gelation as indicated by a “move” back towards the gel point but not beyond the gel point as schematically shown in Figure 3.8a. The reverse gelation moves past the gel point when size reduction and yielding get applied both.

**Figure 3.8:** Traditional linear viscoelastic response of soft solids, including physical gels, below and above their gel point, $p_c$. In this study, the “virgin” sample is defined as a stress-free sample containing non-reduced clay (blue circles). Through size reduction (red squares) (without yielding) or yielding (green triangles) the sample is pushed closer to its gel point and thus increasing relaxation times. The superposition of the virgin sample, the yielded sample, and size reduced solids are shown in Figure 3.8b. The combination of yielding and size reduction (grey star) the sample past its gel point and allows it to flow.

The above discussion is an attempt to understand the low frequency regime observed in Figures 3.5 and 3.6. The convergence of the modulus in the high frequency regime still needs further explanation. The high frequency regime probes small length scales. We believe that as frequency is increased, the contribution of the single layered elastic clay platelets (exfoliated throughout the polymer matrix) begin to be amplified. The
phenomena should be independent of interactions between the polymer and clay (along with clay-clay and polymer-polymer interactions). The dashed lines in Figures 3.5 and 3.6 clearly show the transition from this high frequency regime and the connectivity regime below some critical frequency. This behavior is observed in all the LV material functions. The two regimes in Figures 3.5 and 3.6 (above and below the dashed line) provide two different insight into the role of platelets.

3.5 Conclusions

Polybutadiene/clay composites of varying platelet size were characterized in the linear viscoelastic regime. The composite is a soft physical gel, which was found to reduce its internal connectivity with decreasing particle size. Additional shearing beyond the yield stain induces a solid to liquid transition, as found with SAOS at low frequencies and in creep experiments. The rheology of platelet size reduction can be viewed as a reverse gelation, which depends both on particle size and particle orientation via yielding. In contrast, the high frequency regime of the composite was found to be fairly independent of particle size highlighting the importance of probing sample structures at varying sizes and length scales.
CHAPTER 4
TUNING POLYMER/CLAY NANOCOMPOSITE THROUGH HYDROXYL GRAFTING

4.1 Introduction
A great deal of interest in polymer/clay nanocomposite fabrication emerged after researchers from Toyota demonstrated a 3-fold increase in modulus due to clay intercalation (Kojima 1993). The clay reinforcement of the relatively soft polymer matrix is increased due to intercalation/exfoliation, with exfoliation being the most desirable (Ray 2002). Intercalation/exfoliation can only be achieved when the polymer and clay have some affinity for each other which allows the components to mix. Due to the hydrophilicity of clay, exfoliation is difficult to attain with hydrophobic polymers. Approaches to introduce favorable interactions rely on a compatibilizer, typically a polar oligomer, (Kawasumi 1997) or using co-polymers with polar and non-polar repeat units as the polymer matrix (Wang 2001) with the latter being used in this study. To incorporate polar functional groups, post-polymerization can be performed on homopolymers to create random co-polymers through chemical reactions such as thiol-ene click (Hoyle 2010).

David and co-workers have used thiol-ene click chemistry to graft various heterofunctional thiol molecules to a polybutadiene (David 2008). If an appropriate functional group is incorporated in one of the copolymers, it can interact with a nanofiller. Incorporation of these functional group can also alter the polymer melt’s (before the addition of particles). A well-studied example is the effect of adding hydrogen bonding groups to the polymer’s backbone which has major consequences on the polymer’s linear viscoelastic properties (de Lucca Freitas 1987, Müller 1995, Lewis
Stadler and de Lucca Freitas grafted urazole groups to a polybutadiene matrix and observed increased connectivity and relaxation times as the number of hydrogen bonding groups increased. These changes stem from the increased polymer-polymer interactions and is reflected in changes in other physical properties, such as the glass transition temperature (Müller 1995, Lewis 2014).

Mixing of an appropriate polymer/particle system can provide connectivity (increase in modulus). The origin of the connectivity in polymer/clay composites could stem from either polymer-clay interactions or clay-clay interactions, both of which have been reported in literature. Polymer-particle interactions via hydrogen bonding have been reported in both polyurethane and polycarbonate polymer/composites have resulted in an increase in mechanical properties (Lee 2003, Tien 2000). Particle-particle interactions have also been reported in a PP/clay nanocomposite which formed a “house of cards” structure (Okamoto 2001). This is believed to be driven by electrostatic interactions between the positively charged edges (hydroxyl groups) of the clay compared to its negatively charged surfaces (Lagaly 2003, Tombácz 2004, Tombácz 2006). In both cases, major connectivity is introduced and has the potential to form a percolating network from the physical bond (electrostatic or hydrogen bonds) at sufficient loadings.

In 2004, Sun and co-workers demonstrated the exfoliation of organically modified montmorillonite clay (oMMT) with liquid polybutadiene end-functionalized with either hydroxyl or carboxyl terminated groups (Sun 2004, Chen 2005). Exfoliation was realized with just mild annealing which lead us to term the process the “self-exfoliation” process. The self-exfoliation of oMMT can be achieved even when diluting the number of functional groups by mixing a non-functionalized, non-interacting polybutadiene with the
end-functionalized polybutadiene (Wang 2009, Tanna 2017). While it is known the presence of these groups is critical for exfoliation, a detailed understanding of the exfoliation process is lacking.

In this study, hydroxyl groups were randomly grafted to polybutadiene to promote its interactions with clay. Selecting thiol-ene click chemistry allowed for the systematic vary variation of the functional group concentration to understand its role in the self-exfoliation process. A detailed analysis was developed to understand the connectivity the hydroxyl groups introduced to the polymer matrix itself (polymer-polymer interactions). Developing this analysis, allowed us to focus on the connectivity arising from the clay after composite fabrication. Based on the results from this work, intercalation is believed to be governed by the presence of functional groups in the system and exfoliation governed by the mobility of the polymer.

4.2 Experimental

4.2.1 Materials

The nanocomposites comprised of clay and polybutadiene (PB). Mercaptoethanol was grafted onto low (24% 1,2 addition) and high vinyl (84% 1,2 addition) PB with \( M_n = 5,000 \) and 2,150 g/mol respectively. The reaction was performed in tetrahydrofuran (THF) (Fisher Scientific) with hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (Sigma) serving as the photo-initiator. The same organically modified montmorillonite (oMMT) clay particles (Fenghong Clay Corporation) and antioxidant (Irganox B225 from BASF) were used all the composites.
4.2.2 Grafting Synthesis Procedure

2-mercaptoethanol was grafted onto the high vinyl PB using a standardized procedure. First, two grams of PB, 10 wt% photo-initiator, and varying amounts of 2-mercaptoethanol were dissolved into 10mL of THF. The solution was purged with nitrogen for 15 minutes and exposed to 365nm UV light for 3 hours. The resulting polymer was precipitated into deionized water and dried under vacuum at 65°C for two days to remove residual solvent. The molar ratio of polymer with respect to 2-mercaptoethanol was varied between 0 and 5.2 mM, see Table 1. Grafting to the low vinyl PB needed to be performed at a reduced photo-initiator concentration of 0.6 wt% (with respect to polymer) and at a higher THF solvent concentration of 250mL to avoid interchain crosslinking.

4.2.3 Instrumentation

The molecular weight of the grafted PB was characterized with a THF gel permeation chromatographer and \(^1\text{H}\) NMR spectroscopy in deuterated chloroform. The grafted polymer’s glass transition temperature \((T_g)\) was measured with a TA Instrument Q200 DSC. A stress-controlled Malvern Kinexus Pro+ with a 20-mm parallel plate fixture was used for linear viscoelastic (LV) measurements. Medium angle x-ray scattering (MAXS) in a Ganesha 300 XL SAXS instrument characterized the spacing between clay sheets.

4.3 Results

4.3.1 Grafting of Hydroxyl Groups

PB’s double bonds were reacted with 2-mercaptoethanol using thiol-ene click chemistry. The synthetic procedure for grafting the small molecule is shown in Scheme
4.1. The grafting performed here is random, where some chains remain without grafts and some with higher grafting than the reported average grafting density. $^1$H NMR was used to quantify the grafting density by measuring the ratio of the protons alpha to the hydroxyl group repeat units relative to the remaining unreacted double bonds as listed in Table 4.1. Molecular weights and dispersities in Table 1 are based on the gel permeation chromatography (GPC). As expected, increasing the 2-mercaptoethanol initial concentration increased the grafting density and molecular weight; less expected was the increase in dispersity. Potential reasons for this will be addressed in the discussion section.

**Scheme 4.1:** Synthesis of grafted PB with 2-mercaptoethanol

<table>
<thead>
<tr>
<th>Thiol input (mM)</th>
<th>PB vinyl input (mM)</th>
<th>% Vinyl converted$^a$</th>
<th>$M_n$ (g/mol)$^b$</th>
<th>Disperisty$^b$</th>
<th>$T_g$($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>74</td>
<td>0</td>
<td>5,000</td>
<td>1.57</td>
<td>-25</td>
</tr>
<tr>
<td>0.57</td>
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<td>1</td>
<td>5,100</td>
<td>1.81</td>
<td>-22</td>
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<tr>
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<td>74</td>
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<td>1.71</td>
<td>-14</td>
</tr>
<tr>
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<td>74</td>
<td>6</td>
<td>5,900</td>
<td>1.81</td>
<td>-9</td>
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<td>74</td>
<td>7</td>
<td>5,900</td>
<td>1.81</td>
<td>-6</td>
</tr>
<tr>
<td>5.13</td>
<td>74</td>
<td>8</td>
<td>6,100</td>
<td>2.01</td>
<td>-2</td>
</tr>
</tbody>
</table>

Table 4.1: Concentrations of 2-mercaptoethanol and polybutadiene to generate the polymer series along with tabulated values from $^1$H NMR, GPC, and DSC. a indicates measurements were obtained via $^1$H NMR, b via GPC, and c from DSC.

### 4.3.2 Characterization of Polymer Melt

Hydroxyl grafting caused PB’s glass transition, $T_g$, to increase significantly (Table 4.1). At the highest level of grafting (8% mol grafting), $T_g$ increased by 25K. The increase in $T_g$ and decreased polymer mobility is attributed to increased interchain interactions.

The linear viscoelastic (LV) response of the series of grafted polymers were characterized with SAOS master curves in Figure 4.1. The storage modulus (Figure 4.1a), loss modulus (Figure 4.1b) and complex viscosity (Figure 4.1c) all increased with increasing hydroxyl grafting. This again can be related to the increased polymer-polymer interactions which introduce additional connectivity. Each of the polymers still exhibits traditional terminal flow behavior ($G'\sim w^2$, $G''\sim w^1$ and a zero-shear viscosity) and the typical features of an unentangled, viscoelastic polymeric liquid. Relaxation times were also found to increase with hydroxyl grafting. All the polymer’s LV properties appeared to be similar based on their moduli having similar shape.
The grafted polymers are difficult to compare since each have a different $T_g$. Thus, the reference temperatures were adjusted to maintain a constant distance away from $T_g$, to place equal emphasis on $T_g$ effects. Specifically, each polymer’s reference temperature was adjusted to find the best superposition possible using the neat PB as reference. Doing so resulted in all the LV curves collapsing onto a single curve (Figure 4.2a,b). Based on this successful superposition, a new glass transition temperature was calculated based on the liner viscoelastic data, $T_{g,rheo}$. This is defined as $T_{g,rheo} = T_{g,PB,DSC} + \Delta T_{superposition}$. Figure 4.2c compares these values against the DSC $T_g$. A remarkable agreement was found between the two temperatures. Thus, it can be said that the increase
in LV properties are directly associated with changes in $T_g$.

![Figure 4.2](image)

**Figure 4.2**: Collapsed SAOS master curves when shifting the reference for the storage and loss modulus (Figure 4.2a) and complex viscosity (Figure 4.2b). $T_{g,rheo}$ and $T_g$ from DSC are plotted as a function of grafting density (Figure 4.2c).

4.3.3 Separating Grafting from Hydrogen Bonding

It was unclear whether $T_g$ increased so drastically because of the grafting or hydroxyl functionality of the grafts. To answer this, mercaptobutane, a molecule with no hydroxyl group, was grafted to the PB matrix at a 4 mol% grafting density. Figure 4.3 compares the LV properties of mercaptobutane grafted PB with the neat PB (Figure 4.3). Both polymers had similar viscoelastic properties and the same $T_g$ (-25°C) through DSC.
Thus, changes in $T_g$ are due to the hydrogen bonding of the hydroxyl groups, not the grafting itself.

4.3.4 Addition of Clay to the Modified Polymer

Nanocomposites were fabricated with the grafted polymers. As described earlier, stress-free nanocomposites were generated by having structure formation occur in the rheometer by annealing for 10 hours at 80ºC. Once the structure was developed, SAOS master curve measurements were carried out. SAOS master curves of the composite’s storage modulus/tan $\delta$ (Figure 4.4a), loss modulus (Figure 4.4b), and Winter plot (Figure 4.4c) at various hydroxyl grafting densities are shown in Figure 4.4. Each composite formed a physical gel marked by a plateau in the storage modulus and a downturn in tan $\delta$. The Winter plot provides complimentary evidence of solid structure marked by the straight vertical line observed in the low modulus/low frequency regime (Winter 2009). All composites were plotted at a reference temperature of $T_{g,\text{rheo}} + 45\text{K}$ to place an equal emphasis on $T_g$ effects.

**Figure 4.3:** SAOS master curves of neat PB and a 4 mol% PB grafted with mercaptobutane. The $T_g$ and LV response of the mercaptobutane grated PB matched that of the neat PB at the same reference temperature of 20ºC.
Figure 4.4: The linear viscoelastic response of the grafted PB/clay nanocomposites. The composite’s storage modulus, tan δ (Figure 4.4a), loss modulus (Figure 4.4b), and Winter plot (Figure 4.4c) are shown. A decrease in connectivity is seen at high hydroxyl grafting. Surprisingly the samples with the highest (black) and the second the highest grafting densities (black) exhibited the lowest and second lowest connectivity, i.e. the lowest modulus in the low frequency regime. The decrease in connectivity indicates a decrease in the (physical) crosslinking density. At low and intermediate grafting densities, the modulus in the low frequency regime was higher and appeared to be independent of grafting density. Therefore, an optimal range of hydroxyl grafting exists to obtain maximum reinforcement, above which properties a loss in connectivity is observed.
X-ray scattering was used to determine if the clay was exfoliated in all the composites (Figure 4.5). MAXS revealed that exfoliation only occurred at low grafting densities. At high grafting densities a first order peak appears, and then eventually higher order peaks associated with the spacing between clay sheets, i.e. intercalated clay. We attribute the decrease in connectivity due to the decreased exfoliation. This could either be due to the concentration of hydroxyl groups or decreasing molecular mobility of the starting polymers due to their high $T_g$.

![Figure 4.5](image)

**Figure 4.5**: The plateau modulus of each sample at various grafting densities (Figure 4.5a). X-ray scattering profiles of composites at various hydroxyl grafting densities after structure formation in the rheometer (Figure 4.5b). Highly grafted composites have a lower extent of exfoliation marked by the appearance of a peak (even higher order peaks). All experiments contained at 8wt% clay.

4.3.5 Separating Mobility and Functional Group Concentration

The decrease in connectivity could either be due to increasing $T_g$ effects or hydroxyl group concentration. To address this, a low $T_g$, highly grafted PB was needed. This was done by changing the starting polymer. It is well established that decreasing the amount of vinyl content (24% 1,2 addition) in PB lowers $T_g$, and thus increases molecular mobility (Vinogradov 1970). The initial PB, prior to grafting, in the previous section had a high vinyl content (84% 1,2 addition), meaning it started with a relatively high $T_g$ and
low mobility. The new starting PB could be used while remaining far from its $T_g$. Mercaptoethanol was grafted onto the PB’s backbone at 9 mol%. Figure 4.6a compares the complex viscosity of the neat and grafted polymers at 20°C. The viscosity of the low vinyl, highly grafted PB is even lower than the high vinyl neat PB (no grafts). Thus, the polymer is highly mobile and highly grafted. SAOS master curves of the two grafted polymers along with the neat high vinyl PB are also shown in Figure 4.6b.

![Figure 4.6: Complex viscosity (Figure 4.6a) and SAOS master curves (Figure 4.6b) of the high vinyl, 8% grafted (gray), high vinyl, no grafting (blue), and low vinyl, 9% grafted, and low vinyl, no grafting (green) PB samples.](image)

Clay (8wt%) was added to the polymer to again create stress-free nanocomposites in the rheometer. The dynamic moduli, Winter plot, and MAXS scattering profile of the two grafted polymer/clay nanocomposites are compared in Figures 4.7a-c respectively. The high vinyl polymer nanocomposite has a higher modulus in the high frequency regime and spans over a larger frequency range as it approaches the glassy state. The glassy region is out of the frequency range of the low vinyl PB composites. In the low frequency regime, the low vinyl composite’s storage modulus is greater, specifically the plateau modulus which is particularly evident in the low modulus portion of the Winter plot (Figure 4.7b). This corresponds to higher connectivity and, in this case, a higher
physical crosslinking density. When comparing the MAXS scattering profiles, the low vinyl polymer nanocomposite achieves a higher degree of exfoliation, correlating nicely with the rheology data.

**Figure 4.7:** The dynamic modulus (Figure 4.7a), Winter plot (Figure 4.7b), and MAXS scattering profiles (Figure 4.7c) of the highly grafted nanocomposites with different vinyl content.

**4.4 Discussion**

In our study, we grafted hydroxyl groups to a polybutadiene backbone to promote the polymer’s ability to intercalate/exfoliate clay. Exfoliation was achieved at hydroxyl functionalities as low as 1 mol%, which corresponds to having approximately 1 hydroxyl group per chain, on average. It should be noted, our chemistry produces polydisperse
grafting meaning some chains may have 0 grafts and some multiple. The ability to exfoliate the clay at such a low concentration of functional groups agrees with the findings of Wang and co-workers who showed a blend of non-functionalized and hydroxyl functionalized PB was sufficient for achieving exfoliation (2009). It also appears that LV properties at low to intermediate grafting densities, are independent of hydroxyl grafting. As we go to higher grafting densities, there was a decrease in connectivity along with a transition from clay exfoliation to intercalation. This provides some insight into the self-exfoliation process which will be addressed later in this section.

A consequence of the hydroxyl grafting was that the polymer’s molar mass increased, as expected (David 2008, Wu 2014), along with the dispersity. The grafting of the mercaptoethanol more than doubles the molecular weight of a backbone repeat unit. However, the grafting of the heavy group does not fully account for the 20% increase in molecular weight observed. We suspect an additional side reaction may have occurred. More than likely, the side reaction is due to interchain crosslinking between the double bonds in PB (David 2008). This assumption is supported by the asymmetric broadening in the GPC traces of the grafted polymers. This indicates that some individual chains are growing in molecular weight, presumably due to chain coupling which would account for both the molecular weight and dispersity increase. There appears to be no correlation between the broadening of the GPC peak (related to dispersity) and grafting density. However, since all polymers remained soluble and exhibited terminal flow behavior over the entire frequency range tested, any side reactions that may occur are negligible and have no major consequences in this study.
Hydroxyl groups are known to be capable of hydrogen bonding which introduced additional polymer-polymer connectivity. This in turn decreased chain mobility. The increase in $T_g$ had major implications on the sample’s LV properties with, the overall connectivity and characteristic relaxation times increasing. This type of rheological response has been reported for several hydrogen bonding systems (de Lucca Freitas 1986, Stadler 1988, Lewis 2014). To account for the decrease in mobility, polymer melts were referenced by keeping the same distance away from $T_g$, $(T_g + 45K)$ for all samples. This was an effective method to account for $T_g$ and resulted in the polymer’s LV curves superimposing onto a single curve. Establishing this analysis was critical when adding clay to these polymers. A similar approach for how to account for $T_g$ has been reported by Wagner for PS/PS oligomer blends (2014).

A key aspect of this work was to understand the connectivity clay provided to the polymer matrix, independent of $T_g$. Therefore, SAOS master curves were shifted a set distance above $T_g$ for each sample to equally emphasis the LV contributions of $T_g$. The validity of this approach is verified by the high frequency response of the composite. In this regime, the SAOS master curves converge as they approach the glassy state since they are all an equal distant away from $T_g$. The overall connectivity in the material was evaluated by focusing on the low frequency behavior. Specifically, we focused on the gel’s plateau modulus since it directly correlated to the (physical) crosslink density of the gel. At low to intermediate grafting densities, the overall connectivity was almost constant and showed successful clay exfoliation. This suggests the location of the hydroxyl groups (end-terminated versus grafted) is not critical for exfoliation.
To address whether exfoliation was limited by mobility or functional group concentration, a highly grafted (9%), highly mobile PB was synthesized. Low vinyl PB is well-known to have a low $T_g$ allowing it to maintain a high mobility even at high grafting densities (Vinogradov 1970). Clay was added to low vinyl, highly grafted PB and the composite’s microstructure and LV properties were compared. The highly grafted, highly mobile PB was in fact able to exfoliate the clay and had higher connectivity. This clearly allows us to claim that clay exfoliation is mobility limited, not due to the functional group concentration. Figure 4.4 can allow us to determine a critical viscosity needed for exfoliation. This value falls between 3-3.5 Pa*s.

We believe the self-exfoliation of oMMT into a polybutadiene matrix consists of a two-step process of first clay intercalation and then exfoliation. The first relies on selecting a mobile polymer which can interact with the clay. In our study, this was achieved through grafting hydroxyl groups to the polymer’s backbone. This results in clay intercalation and introduces major connectivity into the composite. The second step relies on the polymer’s ability to diffuse in between the clay sheets to exfoliate them. This is governed by the polymer’s overall mobility (Figure 4.7). If the viscosity of the starting polymer is too high, it will remain in a trapped state and be unable to diffuse through the clay sheets. Exfoliation of the clay provides some additional connectivity to the system but not as much as during intercalation. This stems from the increased effective volume fraction of the clay. We believe the connectivity is driven by particle-particle, not polymer-particle interactions. The Archer group has modified silica surfaces in a PEO matrix and shown that connectivity is only realized when there are appropriate interactions between these particles (Zhang 2002). As they increased the particle loading
of the appropriately modified surface, the connectivity increased. Since our connectivity remained relatively constant at low and intermediate loadings, we believe our case to be driven by particle-particle interactions and may be forming a house of cards structure (Okamoto 2001). Further experiments to address this will be considered.

4.5 Conclusion

We have extended the self-exfoliation of clay from the previously studied end-functionalized commercial polybutadiene. This was proved by randomly grafting hydroxyl groups to the polybutadiene’s backbone which was still able to exfoliate clay. The hydroxyl grafting raised the polymer $T_g$ which affected the LV properties of the polymer. This in turn lowered the polymer’s mobility. Through working with highly mobile, highly functionalized PB, we showed that the process can be limited by mobility, presumably due to the polymer’s ability to diffuse between the clay sheets. These findings present key processing and design considerations if this process were to be extended to high molecular weight polymers.
5.1 Introduction

The self-exfoliation process has been limited to low molecular weight polybutadiene. With appropriate thermal treatment and clay loading, a soft solid physical gel with a modulus on the order of kPa can be formed when the clay is exfoliated. However little work has been devoted to extending the platform to develop tougher rubber composites through either chemical or additional physical (entanglements) crosslinks. A natural industrial advancement of the platform would be to crosslink the polybutadiene, a process performed extensively in the tire industry. The end-functionalized polybutadiene has two obvious crosslinking points. The first is the telechelic polymer end-groups which could be used to perform a polycondensation reaction with the hydroxyl or carboxyl groups (Nor 1998). The second is chemical (radical) crosslinking of the double bonds in the backbone (Coran 2003). An added side benefit of radical crosslinking is the library of commercial initiators capable of being either thermally or photo activated (Odian 2004).

One prior study has has explored chemical crosslinks by performing end-linking with the polymer’s hydroxyl groups to end-link the polymer/clay composite (Bae 2013). In their study, a urethane bond linkage was formed by mixing isophorone diisocyanate (f=2) with exfoliated HTPB/clay composite (f=2). This chemistry was used to form a thermoplastic elastomer (Legge 1987). The fabrication was carried out using a three-step process: first was exfoliating the clay, then mixing HTPB/clay with the crosslinker
(which probably caused the sample to yield), and finally performing a second anneal to crosslink. They found the storage modulus doubled during the chemical crosslinking reaction. While it is unknown how to interpret the competition between the crosslinker and clay interaction with the polymer’s hydroxyl terminated end groups, the study demonstrated a steady increase in linear-elastic mechanical properties at all clay loadings tested (up to 15wt%).

This work aims to extend the work by Bae and co-workers. We decided to use the polybutadiene’s double bonds to UV crosslink with thiol-ene click chemistry (Hoyle 2010). By opting to do this, we realized two additional benefits of the system. First, was the ability to create a tougher matrix material due to the higher concentration of double bonds compared to that of the telechelic end groups. Secondly, is the ability to use a one-step mixing process with the first step being exfoliation (thermal) and the second crosslinking (UV light). We found that we were able to achieve a significantly higher chemical crosslink density with chemical crosslinking dominating the reinforcement provided by the clay.

5.2 Experimental

5.2.1 Material

Dicarboxy terminated polybutadiene (CTPB), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), and hexane dithiol were purchased from Sigma-Aldrich. oMMT is the same referenced earlier.

5.2.2 Sample Preparation

Crosslinked CTPB/clay thermosets were prepared by solubilizing the DMPA (1.5 wt% with respect to CTPB) into hexane dithiol (3 wt% with respect to the CTPB). Once
fully dissolved, the CTPB and oMMT were mixed together (8 wt% with respect to CTPB). The materials were then homogenized in the mixer at 3000 RPM for 1 minute causing the solution to assume a cream color. The mixture (still a liquid) was quickly poured into a circular mold between a sheet of Kapton and a quartz disk. The entire assembly was then annealed at 80°C for ten hours to allow the clay to exfoliate at which point the sample turned transparent. This provides qualitative evidence that intercalation/exfoliation has occurred. The sample was then exposed to UV light for 3 hours with the UV transparent quartz facing the light. The sample was then rotated and kapton sheet was peeled off to expose the opposite side of the sample to the UV light for an additional 3 hours. This was then followed by a 1 hour anneal at 80°C. This completed the exfoliation and crosslinking procedure without any shear being placed on the sample until it was crosslinked. Crosslinked samples of the same composition (without clay) were prepared and were subjected to the same procedure. Samples containing exfoliated clay and no crosslinks were exfoliated in the rheometer at 80°C for eight hours, as described earlier.

5.2.3 Instrumentation

Rheological measurements were carried out using a stress-controlled rheometer with a 20 mm parallel plate fixture. The crosslinked samples had a normal force of 2.5N applied during the frequency sweeps unless otherwise specified. The samples with no crosslinks were set to a constant gap height of 1mm throughout the entire rheological measurement. Mass/volumetric swelling tests were performed on the crosslinked samples by soaking them in chloroform for 7 days. Volumetric changes in the samples were
measured using Zeiss Axiovert 200 optical microscope. Samples were dried for 4 additional days to determine the mass of the gel after deswelling.

5.3 Results

5.3.1 Fabrication of Thermoset

This study uses thiol-ene click chemistry to crosslink the polybutadiene matrix (Doyle 2004). The synthetic scheme used in this study is shown in Scheme 5.1. To quantify the extent of crosslinking, we assume that only vinyl (1,2 addition) PB reacts since 1,2 vinyl PB is over ten times more reactive than 1,4 polybutadiene (cis/trans) (Brummelhuis 2008). This stems from the vinyl groups being pendent and thus having less steric hindrance. $^1$H NMR of the neat CTPB (before crosslinking) was used to quantify the ratio of vinyl to cis/trans PB which was found to contain about 26% vinyl. (Figure 5.1). This on average means there are approximately 20 vinyl double bonds per polymer chain ($f=20$) which we expect to react with the hexane dithiol ($f=2$).

Scheme 5.1: Synthetic scheme used to crosslink the CTPB which used UV activated thiol-ene click chemistry.
A careful fabrication process was developed to create the clay reinforced thermoset. The main object was to ensure exfoliation occurred before crosslinking. To determine if this was achieved, x-ray scattering profiles were taken at various steps in the sample fabrication process. As expected, the neat clay’s $d_{\text{spacing}}$ (Figure 5.2, black) was found to be 2.1nm. After mixing the clay/CTPB/crosslinker, a broad peak centered about 11.1nm appeared (blue). This is due to the intercalation of clay which occurred even though it was only exposed to room temperature for a minimal amount of time. A slight peak at 2.1nm still remains indicating some clay still maintains its initial spacing. After the annealing (green) and crosslinking steps (red), both the peaks disappeared indicating the clay had been exfoliated throughout the polymer matrix. This proves our fabrication process allows exfoliation to occur first, followed by crosslinking and that the crosslinking does not prevent exfoliation.

Figure 5.1: $^1$H NMR used to quantify the ratio of vinyl to cis/trans in the CTPB.
5.3.2 Varying Normal Force during Rheology

When performing LV measurements on the crosslinked samples, normal force needed to be applied to achieve reproducible rheological data. Applying a normal force ensures proper contact is made between the sample and the plate fixtures. Since the crosslinked samples are solids, there was no risk of the sample flowing out or any plastic deformation at the normal forces used here.

To better understand the effect of normal force, isothermal SAOS frequency sweeps were performed at different normal forces. Figure 5.3a shows the measured gap height after having applied a pre-subscribed normal force and Figure 5.3b the corresponding frequency sweeps measured at that normal force. In the low normal force regime, an exponential change in gap height is observed as the normal force is increased. As the normal force is increased further, a linear relationship is then observed between the two. We believe this is strong proof that proper contact is established between the plate and the sample. This also agrees nicely with the SAOS frequency sweep data. At low normal forces, the complex modulus, $G^*$, rose with increasing normal force.

**Figure 5.2**: Scattering profiles at various steps during sample fabrication: neat clay (black), freshly mixed sample (blue), after annealing (red), and after crosslinking (green). Exfoliation was achieved only after annealing indicating separation of exfoliation and crosslinking. Composites contained 8wt% clay.
Eventually at approximately 2N, the modulus becomes independent of the normal force. This indicates perfect contact has been established between the plate and the sample. The linear relationship between normal force and gap height is established at the same force as the complex modulus independence. This proves that normal force is needed for measurements to ensure proper contact between the plate and sample is achieved. The amount of normal force applied, i.e. compression, is small and thus no deformation in the sample occurred. Remaining rheological measurements were measure by applying a normal force of 2.5N of normal force, marked by the data point \((F_0, h_0)\) in Figure 5.3a.

**Figure 5.3:** Gap height as a function of normal force (Figure 5.3a) and corresponding SAOS frequency sweeps at those given normal forces (Figure 5.3b). The SAOS frequency sweeps become independent of normal force at the same point a linear relationship is seen between the gap height and normal force. Remaining rheological measurements were performed at normal force of 2.5N.

### 5.3.3 Rheology

Rheological measurements allow for a quantifiable means to understand the mechanical reinforcement provided by chemical crosslinks and exfoliated clay. SAOS master curves were performed on neat CTPB, CTPB/clay, crosslinked CTPB, and clay filled crosslinked CTPB. Such a comparison allows us to understand the effects of the
crosslinks and the clay individually. Figure 5.4a,b compares the effect of crosslinking. Figure 5.4a compares the samples without clay and Figure 5.4b the samples with clay. The increase in modulus due to crosslinks was much more significant in the samples without clay. This is because clay containing samples already form a percolating network prior to the CTPB/clay forming a physical gel. (Wang 2010). In the case of the samples containing chemical crosslinks, a distinct plateau in $G'$ was seen.

Figure 5.4: SAOS master curves to quantify the rheological effects of chemical crosslinks and clay. Figure 5.4a compares the neat CTPB to crosslinked CTPB while Figure 5.4b does the same for the filled systems.

Figure 5.5 show the mechanical reinforcement provided by the clay. It can be seen that the effect of oMMT is significant at high frequencies while the crosslinks dominate at low frequencies (the storage modulus of the two samples converge). This indicates of the crosslinking density (comparing chemical to physical) is dominated by the covalent bonds, not physical bonds from the clay.
During the LV measurements above, it was assumed that all the samples were in a steady-state and no further chemical changes occurred during SAOS frequency sweeps. To determine the validity of this assumption, Booij-Palmen plots for the 4 samples above were constructed in Figure 5.6a (van Gurp 1998, Trinkle 2001). Samples are considered thermorheologically simple if they collapse onto a single curve in the Booij-Palman, prior to applying time temperature superposition. Each individual sample imposed nicely upon each other, indicating thermorheological simplicity. Despite being tested over a large range of temperatures (T: -10-80°C), the chemically crosslinked samples span a smaller range than both CTPB and CTPB/clay. This will be addressed in the discussion. Shift factors for the 3 samples are also shown in Figure 5.6 for the data presented in Figure 5.4a. Free shifting was used to generate these master curves with the horizontal shift dominating.

Figure 5.5: SAOS master curves of the CTPB crosslinked with and without clay. The LV response of the two thermosets appear to similar expect at high frequencies
5.3.4. Swell Tests

The chemically crosslinked samples were swollen in chloroform to compare the effect clay has on swelling. Both mass and volumetric swell tests were performed to ensure the two correlated. To justify the assumption of isotropic swell, all samples were measured in two directions (length and width) and averaged to calculate the volumetric swelling. In addition, the masses of deswollen samples were also taken. Table 5.1 summarizes the results from swelling experiment. It was found that the samples containing clay swelled slightly more than the samples without clay despite seeming to have a higher modulus. In addition, it was shown that samples containing clay were deswollen more than that of the neat crosslinked composite. This will be addressed in the discussion section.
<table>
<thead>
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<th>$M_S/M_D$</th>
<th>$V_S/V_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No clay</td>
<td>10.2</td>
<td>0.798</td>
<td>5.35</td>
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<tr>
<td>With clay</td>
<td>11.9</td>
<td>0.784</td>
<td>6.75</td>
</tr>
</tbody>
</table>

**Table 5.1:** Results from the swelling experiments for the crosslinked CTPB with and without clay in chloroform. $M_s$ is the swollen mass, $M_0$ is the initial mass, $M_D$ is the deswollen mass and $V$ represents volumetric values opposed to mass.

5.3.5 Differential Scanning Calorimetry

As additional connectivity is added to the system (from both clay and crosslinks), we expected the polybutadiene’s $T_g$ to shift as well. Only a minimal change in $T_g$ was seen for the clay (~0.5°C) while the chemical crosslinks were found to have a much more pronounced shift in $T_g$ (~8 °C). Similar changes in $T_g$ have been observed due to crosslinking (Ueberreiter1950, Fox 1955). We expect that the clay does not have any major effects on the polymer’s mobility.

**Figure 5.7:** DSC thermograms for the neat CTPB (black), CTPB/clay (red), CTPB crosslinked (blue), and CTPB crosslinked with clay (green). Only crosslinking was found to have a major influence on $T_g$.  

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5.4 Discussion

We successfully designed a method to fabricate a clay reinforced crosslinked thermoset using the self-exfoliation process. We wanted to avoid yielding the composite during sample preparation and secondly, to use only a one-step mixing process to prepare the sample. The reason for avoiding shear was based on the yielding work presented in Chapter 2 (Tanna 2017). Yielding would minimize the clay’s reinforcing effect (in the direction of shear) and thus lower the overall LV rheological properties of the final thermoset. It is unclear if this same effect would be seen under uniaxial stress, rather than shear. Our study focused on having the clay sheets exfoliated and randomly oriented throughout the matrix. Once the polymer was crosslinked, we assumed the clay was locked into place and thus would be unable to orient due to the stiffness of the crosslinked polybutadiene matrix. We also wanted to ensure the entire fabrication could be completed using a one-step mixing step. This allows for a more streamlined and simplified process to make the overall fabrication more industrially feasible. This was done by having exfoliation be thermally trigger (governed by the self-exfoliation process) and the crosslinking being UV activated, allowing us to separate the two phenomena. This allowed us to first exfoliate and then crosslink. The ordering of these events was critical because if we were to first crosslink, the polymer would not be able to flow and thus could not mix/exfoliate the clay.

Once the composite fabrication procedure was established, samples were prepared and characterized. Based on comparing the rheological response of the two crosslinked polybutadienes (Figure 5.3), the effect of clay was only realized at high frequencies. In the low frequency regime, the chemical crosslinks dominate. This effect was not seen in
the end-linking study since the functionality of the crosslinker was low (f=2). When comparing the two storage moduli from the two methods, ours (crosslinking) was over an order of magnitude higher in modulus. In the high frequency regime, smaller and smaller length scales begin to be probed. We believe this begins to correspond to the length scale of the individual elastic clay sheets (Vermant 2007). As we approach higher frequencies, these effects being to play a larger and larger role and thus the moduli of the filled and unfilled polymers began to diverge.

The crosslinked samples containing clay also had a higher swelling ratio than the unfilled crosslinked CTPB. Based on Flory-Rehner theory, this corresponds to a lower crosslinking density (Flory 1943). This was initially surprising because rheologically, it appeared the clay filled crosslinked polymers seemed to have a higher modulus over the entire frequency range tested. A higher modulus would indicate a higher crosslinking density as constituted by the well-known Affine type relationship. To further understand this, the two sample’s complex moduli are plotted on a linear scale to focus on the low frequency response (Figure 5.9). Interestingly, a crossover point between the two samples is observed. This would suggest the clay filled sample has a lower crosslinking density. The point at which this occurs is marked by the line drawn in Figure 5.9.
To correlate the swelling and rheological measurements, we realized swelling experiments correspond to the low frequency regime (long time scales). Swollen samples were left in solvent for an extensive period of time (1 week) to allow them to reach an equilibrium. This long-time behavior corresponds to low frequencies (long times) in which the crosslinked samples without clay has a higher modulus. This agrees with the Affine relationship. We speculate that decreased crosslinking density could be due to some of the individual sheets of clay preventing crosslinks from forming. Since the lateral dimensions of the clay sheets are on the order of a micron and are significantly larger than hexane dithiol molecule, angstroms, it is not surprising to think a decrease in the number of crosslinks may occur (Murthy 2002). It should also be noted that we believe the physical crosslinking from the clay has minimal effects in both rheology and swelling experiments. In the case of rheology, this is because the connectivity provided by the clay is orders of magnitude lower than the covalent crosslinks. In the case of swelling, it is because the polymer/clay composite are fully soluble in chloroform and thus would not help hold the sample together when swollen.
The decrease in crosslinking density is also realized in the loss moduli of the crosslinked samples in Figure 5.4. It can clearly be seen that the loss modulus is greater in the clay containing thermosets over the entire frequency range tested. This can be attributed to the decrease in crosslinking density which results in a higher liquid-like response being realized. This could stem from having large dangling chains in which only bound at one point along the backbone or a lower molecular weight between entanglements.

5.5 Conclusion
We have successfully been able to fabricate a crosslinked polybutadiene containing exfoliated clay using a one-step mixing process. This was done by separating the two steps by using thermal and UV light activated triggers to exfoliate and crosslinking respectively. By using the polymer’s double bonds, we were able to achieve much tougher composite on the order of hundreds of kPA. The effect of clay was only realized at high frequencies which we believe beings to correspond to the individual length scale of the clay sheets. Finally, we found the clay prevents some crosslinks from forming by comparing the low frequency regime of the rheological response of the two crosslinked samples. These results agreed with the swelling experiments when the two samples were swollen in chloroform.
CHAPTER 6
FUTURE DIRECTIONS

6.1 Self-Exfoliation to High Molecular Weight Polymers

As previously discussed, the self-exfoliation process has been limited to low molecular weight polybutadiene or infinite molecular weight thermosets (crosslinking the polybutadiene matrix after exfoliation). While there are applications which could rely on the low molecular weight soft solid composite, a future direction would be to extend the platform to high molecular weight, entangled polymers. This would result in connectivity stemming from both the polymer entanglements and the exfoliated clay. However, increasing molecular weight presents additional challenges which need to be considered, especially with regards to its high viscosity and low mobility (Nemoto 1972). Of course, other unforeseen factors may be present but for now, we will address ways to increase the mobility without applying large stresses.

The first and most simple way to ensure there is enough polymer mobility would be to increase the exfoliation temperature. Using a combination of rheology and x-ray scattering, a critical temperature could be identified, the temperature to achieve successful exfoliation. Working at elevated temperature should provide the polymer enough mobility; although the chain dynamics may still be slightly different than the low molecular weight PB. The low molecular weight polymer follows Rouse dynamics while the high molecular weight should follow Reptation type dynamics. If a series of polybutadienes were tested at varying molecular weight, a scaling relationship between critical exfoliation temperature and molecular weight could be developed. Presumably the critical temperature would increase with molecular weight.
A drawback of using these elevated temperatures is polymer degradation may begin to occur. Preliminary unpublished results have shown degradation of PB in the presence of clay can occur at temperatures as low as 90°C. Specifically, the double bonds in the polybutadiene backbone are thermally unstable and may be prone to interchain crosslinking or oxidation. If interchain crosslinking was to occur, this would increase the polymer’s molecular weight and thus lower mobility, essentially recreating the initial problem of low mobility. An additional challenge is how to incorporate functionality into the high molecular weight polymer. The reason low molecular weight PB is end-functionalized is because it is used to create copolymers with soft and hard (low and high $T_g$) segments (Nor 1998). This is not done industrially for high molecular weight polymers. Our previous results have shown that the location of the functional groups is not critical, so functionality could be incorporated using post-polymer modification as done in Chapter 4. Additionally, monomer synthesis could also be performed by copolymerizing 1,5 cyclooctadiene with 5-hydroxy-1-cycloctene at select feed ratios (Bielawski 2000). This would result in functionalized PB with exclusively 1,4 addition, which would have a lower glass transition. Once the kinetics of polymerization are established, different amounts of functionality and degree of polymerization could be synthesized.

Alternatively, a three-component system could be used to exfoliate the clay with all three components being commercially available. The three components would be a high molecular weight non-functionalized PB, a low molecular weight functionalized PB (CTPB or HTPB), and the oMMT previously used. The approach is inspired by the work presented earlier in which a PP modified with maleinanhryde oligomer was mixed with
PP and clay, and used to fabricate a PP/clay composite (Kawasumi 1997). In our case, the low molecular weight PB would be analogous to the PP oligomer. Ideally, it would interact with and exfoliate the clay. The polymer’s backbone structure should also be compatible with the high molecular weight PB since they are same molecular weight species. The low molecular weight end-terminated PB would also help plasticize the high molecular weight PB and provide mobility to the system. Again, due to the mobility restriction, higher temperatures may be needed but not as high as the method presented in the first section..

The final method which may be implored is to add solvent to one of the above-mentioned systems. The role of the solvent would not be to interact with the clay but instead just to provide mobility into the system. The polymer would still be responsible for interacting the clay. The drawback of opting to use this method is the need to add a solvent removal step. While this step is not ideal, it is trivial to remove solvents on a lab scale type process. Minimal solvent should be used since its only role is to add mobility to the system.

Once a high molecular weight system is successfully fabricated to exfoliate clay and verified with x-ray, the rheological properties of these systems should be interesting. In terms of the linear viscoelastic behavior, a key question would be understanding the role of both entanglements and clay. We assume that clay exfoliation at sufficient loadings should still form a physical gel, but needs be experimentally verified. Using SAOS master curves, we would probe the connectivity provided each component, i.e. clay and entanglements. We expect both the clay and entanglements to have unique relaxation process but are unsure whether they will overlap or not. Rheology will be used
to probe and assign relaxation times to both, assuming they can be decoupled. In
addition, exfoliation kinetics could be explored to understand how chain dynamics may
be affect the structure formation in greater detail. Finally, the yielding behavior of this
material should be explored. When the composite is exposed to higher stresses, we expect
the entanglements to increase the yield strain. In fact, two separate softening processes
may occur. The first coming from clay alignment, and the second from shear thinning.
Predicting which of these processes will occur first is difficult but could be measured
experimentally.

6.2 Extension of Clay Reinforced Thermoset Platform

In a previous section, we used the self-exfoliation process to fabricate a clay
reinforced thermoset by crosslinking the polybutadiene after clay exfoliation. However
only the rheological and swelling properties of clay reinforced thermoset were explored.
There remain several different directions this project could be extended with regards to
using different crosslinking chemistries for both fundamental and applied studies.

Crosslinking of polybutadiene has been a heavily explored topic, particularly in
the tire industry. There are a number of well-develop chemistries and commercial
additives which could be used to crosslink the polymer’s double bonds while still
preventing oxidation, after clay exfoliation. In our study, we separated exfoliation and
crosslinking by having non-competing thermal and UV activated mechanisms. An
alternative method would be to use a two-step thermal treatment. The first temperature
would be for exfoliation, between 60-80°C, and the second to thermally crosslink at a
higher temperature. It would be critical to ensure crosslinking does not occur during
exfoliation. This would mirror a vulcanization type process used for rubbers in tire
industry. It would be worthwhile to compare the final properties of a UV and thermally crosslinked polymer and maybe even to compare clay filled versus carbon black polybutadiene nanocomposites.

An interesting fundamental direction of this work would be to use crosslinking to lock in the clay microstructure. This could be used to study intermediate states of the exfoliation process even more. An interesting direction would be to use this to determine if yielding was truly due to clay sheet orientation as we previously speculated. The experiment would go as follows. A CTPB/clay composite could be formed in the rheometer to establish its initial virgin, stress-free state. The sample could then be crosslinked and studied using TEM. A second composite could then be subjected to the same treatment, then yielded and finally crosslinked. This sample could also be studied under TEM. The two states could then be compared. If in fact it yielding is due to clay orientation, the ordering parameter of the clay could be studied as a function of deformation time, strain, strain rate etc. This could be correlated to the LV data from SDS methods. A complete understand of the microstructure and LV properties of the system could then be expressed.

More applied physical properties could also be measured with clay reinforced thermoset, namely non-linear solid mechanical properties and barrier properties. Based on the linear viscoelastic characterization, the effect of clay on the composite was minimal; however, we do not expect this to be the same with non-linear mechanics, especially with regards to fracture toughness (Wang 2005, Zerda 2001, Zilg 1999). For these experiments, compact tension specimen samples would be characterized using a standardized test, ASTM D 5045-96. A comparison between the fracture toughness of the
filled and unfilled polymers could then be made. We expect the clay fillers will increase the crack propagation path by causing it to have to travel around the clay sheets and thus result in a much more tortuous path. Along with the calculated fracture toughness, the path length could also be studied with SEM to understand the possibilities of shear banding and yielding which may occur above and below the percolation threshold.

Finally, we expect there to be major improvements in the barrier properties of the thermoset (Lan 1994, Giannelis 1996, Bharadwaj 2001). We expected this because the diffusion path of the air particles will be increased because they would be unable to pass through the clay sheets. Bharadwaj has modeled the effect of platelet length and orientation on the barrier properties. Based on his findings, orientation plays a key factor but becomes less and less critical as the platelet length increases. His work also suggests exfoliated sheets are the most critical. Basic experiments that could be pursued are comparing the permeability of the filled and unfilled composite along with the permeability as a function of strain, if clay sheets are oriented. The results could then be compared to the proposed model. Alternatively, the model could be used to understand the effect orientation has on the composites final properties. This would be extremely interesting because it would provide a way to understand the effect of shear by exfoliating, shear-oriented yielding, crosslinking and then permeability measurements. If the permeability decreases as a function of strain, it would prove indirect but strong proof of shear orientation.

If both the two project areas are successfully completed, three different classes of materials could be established based on the self-exfoliation platform, including thermosets and thermoplastics. The first would be the soft solid physical gel which was
the focus on the work presented here. The second would be the clay reinforced thermoplastic in which a high molecular weight polymer is used to exfoliate the clay. Finally, the clay reinforced thermoset have already been fabricated and may be extended further.


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