CHAPTER IV

GREEN NANOCOMPOSITES FROM POLYCAPROLACTONE (PCL)/ SOY PROTEIN ISOLATE (SPI) BLEND WITH ORGANOCLAY
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SECTION-I

4.1 SHORT REVIEW ON NANOTECHNOLOGY

4.1.1 Polymer-layered-silicate nanocomposites (PLS)

Layered-silicate-based polymer nanocomposites have received considerable interest over the last decade in research and development as an alternative to conventional filled composites. The unique and improved properties attributed to the nanometer size and high aspect ratio of individual platelet show the features such as greater mechanical strength, barrier property and so on. However to achieve such properties, nanocomposites require high levels of dispersion of the organoclay depending upon chemical affinity between the polymer matrix and the silicate layers of clay. When the polymer-clay interaction is not favorable enough to give well exfoliated aluminosilicate platelets, then intercalated and partially exfoliated structures are usually obtained. Accordingly challenging attempts have been made especially to fabricate exfoliated structured nanocomposites known to show dramatic enhancements in composite performance.

Since PLS nanocomposites achieve composite properties at much lower volume fraction of reinforcement, they avoid many of the costly and cumbersome fabrication techniques common to conventional fiber- or mineral- reinforced polymers. Instead they can be processed by techniques like extrusion and injection molding.

The combination of enhanced properties, weight reduction and low cost has already led to a few commercial applications. Toyota Motor Company has successfully introduced an automotive timing-belt cover made from nylon-layered-silicate nanocomposites. Ube Industries in Japan in collaboration with Toyota is also developing nanocomposites- barrier films for food packaging and other applications.

4.1.1.1 Structure of layered-silicate

Polymer-layered-silicate (PLS) nanocomposites are a hybrid between an organic phase (the polymer) and an inorganic phase (the silicate). The choice of the silicate determines the nanoscopic dispersion typical of nanocomposites. The silicates used in
PLS nanocomposites, like the better known members of the group talc and mica; belong to the general family of 2:1 layered- or pylllosilicates. Their crystalline structure consists of a two dimensional layer obtained by blending two tetrahedral silica laminae with metal atoms (i.e. Mg for talc and Al for mica) to form a corresponding octahedral metal oxide lamina (Fig. 4.1). Each layer is separated from its neighbors by a van der Walls gap called a gallery or interstratum. These galleries are usually occupied by cations that counterbalance the negative charge generated by the isomorphous substitution of the atoms forming the crystal (Mg$^{2+}$ in the place of Al$^{3+}$ in the montmorillonite or Li$^+$ instead of Mg$^{2+}$ in hectorite). These cations are normally hydrated alkaline and alkaline-earth metal cations.

4.1.1.2 Nanocomposites structures

Depending on the nature of the components used (layered-silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when layered-clay is associated with a polymer [Fig. 4.2 (a)]. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite [Fig. 4.2 (a)] is obtained, whose properties stay in the same range as traditional microcomposites. Beyond this classical family of composites, two types of nanocomposites can be recovered. Intercalated structure [Fig. 4.2 (b)] in which a single (and more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [Fig. 4.2 (c)].

4.1.1.3 Preparative techniques

Intercalation of polymers in layered hosts, such as layered silicates, has proven to be a successful approach to synthesize PLS nanocomposites. The preparative methods are divided into three main groups according to the starting materials and processing techniques:
4.1.1.3.1 Intercalation of polymer and pre-polymer from solution (Exfoliation-Adsorption)

This layered-silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwishing the polymer to form, in that case, an ordered multilayer structure.

Using this method, intercalation only occurs for certain polymer/solvent pairs. This method is good for the intercalation of polymers with little or no polarity into layered structures, and facilitates production of thin films with polymer-oriented clay intercalated layers. However, from industrial point of view, this method involves the copious use of organic solvents, which is usually environmentally unfriendly and economically prohibitive.

4.1.1.3.2 In situ intercalative polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

4.1.1.3.3 Melt intercalation technique

There are many advantages to direct melt intercalation over solution intercalation. For example, direct melt intercalation is highly specific for the polymer, leading to new hybrids that were previously inaccessible. In addition, the absence of a solvent makes direct melt intercalation an environmentally sound and an economically favorable method for industries from a waste perspective.

This process involves annealing a mixture of the polymer and OMLS above the softening point (molten state) of the polymer, statically or under shear. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. A range of nanocomposites with structures from intercalated to exfoliate
can be obtained, depending on the degree of penetration of the polymer chains into the silicate galleries.

4.1.1.3.4 Template synthesis

This technique, where the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer-hydroxide-based nanocomposites but is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.
Fig. 4.1 Structure of 2:1 layered-silicate showing two tetrahedral-site sheets fused to an octahedral-site sheet.

Fig. 4.2 Schematics of different types of composite arising from the intercalation of layered-silicates and polymers (a) phase separated microcomposite, (b) intercalated and (c) exfoliated polymer/layered-silicate nanocomposites.
4.2 GREEN NANOCOMPOSITES FROM POLYCAPROLACTONE (PCL)/SOY PROTEIN ISOLATE (SPI) BLEND WITH ORGANOCLAY

4.2.1 INTRODUCTION

Green polymers in conjunction with nanotechnology are poised to create a major breakthrough in plastic-based industries. Biobased economy is challenging to agriculture, forest, academia, government and industry. There is growing urgency to develop and commercialize natural resource-based new materials and innovative technologies for sustainable development of our society. The high as well as unstable price of petroleum, the growing environmental need of national security are some of the driving forces in looking towards natural based plastics and materials. Renewable-resource-based bioplastics like polylactic acid (PLA), polyhydroxyalkanoates (PHAs), cellulosic plastics, soy protein plastics and starch plastics are moving towards mainstream. This has opened up new market opportunities for developing biodegradable and biobased products as the next generation of sustainable materials that meets ecological and economic requirements(1).

For these reasons, throughout the world today, development of biodegradable materials with controlled life-span and desired properties has been a subject of great research challenge to the community of materials scientists and engineers. Among biodegradable polymers, synthetic biodegradable polymers derived from the petroleum sources such as polybutylene succinate and polycaprolactone have been commercialized due to their good processability with fairly good mechanical and physical properties. But, cost of the petrobased aliphatic polyesters is high, which restricts their extensive applications. Soy protein is regarded as an alternative material to nondegradable petroleum plastics because they are abundant, renewable, less expensive and biodegradable. But, the application of soy protein plastic is limited because of its low strength and high moisture absorption (2, 3). Therefore, blending of the petrochemical-based aliphatic polyesters with agro-based soy protein is an effective way to reduce the cost of the biodegradable materials.
Nanoreinforcements of biodegradable polymers have strong promise in designing eco-friendly green nanocomposites. The reinforcing material has the dimensions in nanometric scale in these nanocomposites. Among various nanoreinforcements currently being developed, layered silicate clay mineral are most widely used as the reinforcing phase due to its easy availability, low cost and more importantly, its environmentally benign nature (4, 5). The reinforcement efficiency of these nanocomposites, with very low level of nanofiller incorporation (≤5 wt %), can match that of conventional composites with 40–50% of loading with classical fillers due to high aspect ratio and high surface area of the nanolayered clays. Extensive studies on the preparation and properties of biodegradable polymer-clay nanocomposites have been conducted on the basis of several biodegradable polymers including polylactide (PLA), polyhydroxy butyrate (PHB), thermoplastic starch (TPS), polybutylene succinate (PBS), and polycaprolactone (PCL) (6-13). It has been revealed that the clay nanoparticles can enhance mechanical properties, thermal stability, barrier properties and control biodegradation rate of the biodegradable polymers.

Research is being carried out with a series of green nanocomposites based on soy proteins for the development of a new generation of biodegradable polymers with performance-cost-ecology balance. In this study, I prepared polycaprolactone (PCL)/soy protein isolate (SPI)/organoclay ternary nanocomposites by using a melt compounding method. Morphology and the effects of clay nanolayers on mechanical and rheological properties of the nanocomposites were examined.

4.2.2 EXPERIMENTAL

4.2.2.1 Materials

Soy protein isolate (SPI) with protein content about 90% was obtained from Archer Daniels, Midland Co., (Decatur, IL, USA) as gift sample and used for the reaction. Polycaprolactone (PCL), under the commercial name of CAPA 680, was purchased from Solvay Interox Ltd, UK. Clay used in this study is an organically modified montmorillonite clay (Cloisite 30B, Southern Clay Products). This material was prepared by the supplier through ion-exchanging Na⁺ montmorillonite(with a reported cation exchange capacity of 0.95 mequiv/g) with methyl tallow bis-2-
hydroxyethyl ammonium. The tallow used was composed of ca 65% C18, 30% C16 and 5% C14 units.

4.2.2.2 Preparation of PCL/SPI/clay nanocomposites

PCL, SPI and organoclay were dried under vacuum at 80°C for overnight prior to use. A Haake Rheomix 600 internal mixer was used for the preparation of the PCL/SPI/organoclay nanocomposites. The PCL/SPI blend composition was 80/20 wt/wt, and the organoclay content is 1, 2.5, and 5 wt %. The mixing was carried out at 160°C for 12 minutes with a rotor speed of 100 rpm. After mixing, the samples were compressed into 2 mm thick plates for further characterization.

4.2.2.3 Characterization

Change in gallery height of the clay was investigated by WAXD experiments, which were carried out using an X-ray diffractometer (BEDE D-3 system) with Cu Kα radiation at a generator voltage of 40 kV and a generator current of 100 mA. Samples were scanned from 2θ = 1-10° at a scanning rate of 2°/min.

Dispersibility of the silicate layers in the composite was evaluated using transmission electron microscopy (TEM). A TEM micrograph was obtained with JEOL 200 CX TEM using an acceleration voltage of 200 kV (magnification x 160,000).

Tensile tests were conducted at 25°C using a universal testing machine (United Co.STM-10E) at a crosshead speed of 5 mm/min. Dynamic mechanical tests were performed using dynamic mechanical analyzer (TA Instrument DMA 2980). The sample was subjected to a cyclic tensile strain with amplitude of 0.03% at the frequency of 10 Hz. The temperature was increased at the heating rate of 2°C/min in the range of -100°C to 60°C.

Melt rheological measurement was carried out on RMS 800 (Rheometric Inc.). Dynamic oscillatory shear measurement was performed at 100 °C using set of 25 mm diameter parallel plate and a sample thickness 1-2 mm. The frequency sweep was carried out at a frequency range of 0.01-100 rad/sec at a strain of 5 % (it is well within the linear viscoelastic range).
Table 4.1 Basal Spacing of organoclay and PCL/SPI/organoclay nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$</th>
<th>Basal spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organoclay</td>
<td>4.83</td>
<td>18.27</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 wt %</td>
<td>2.40</td>
<td>36.79</td>
</tr>
<tr>
<td>2.5 wt %</td>
<td>2.40</td>
<td>36.79</td>
</tr>
<tr>
<td>5 wt %</td>
<td>2.58</td>
<td>34.16</td>
</tr>
</tbody>
</table>

Table 4.2 Terminal region slope of PCL/SPI blend and its nanocomposite containing 5 wt % clay

<table>
<thead>
<tr>
<th>Clay content (wt %)</th>
<th>Slope of $G'$ (Pa)</th>
<th>Slope of $G''$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.64</td>
<td>0.82</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Fig. 4.3 X-ray diffraction patterns for organoclay and PCL/SPI/organoclay nanocomposites

Fig. 4.4 TEM photograph of PCL/SPI/organoclay hybrids containing 1 wt % of the organoclay
Fig. 4.5 TEM photograph of PCL/SPI/organoclay hybrids containing 2.5 wt % of the organoclay

Fig. 4.6 TEM photograph of PCL/SPI/organoclay hybrids containing 5 wt % of the organoclay
Fig. 4.7 Effect of clay content on the Young’s modulus and tensile strength

Fig. 4.8 Effect of clay content on the elongation at break
Fig. 4.9 Dynamic storage modulus of PCL/SPI blend and its nanocomposites

Fig. 4.10 Dynamic shear elastic modulus of PCL/SPI blend and its nanocomposite containing 5 wt % clay
Fig. 4.11 Dynamic shear loss modulus of PCL/SPI blend and its nanocomposite containing 5 wt % clay

Fig. 4.12 Complex viscosity of PCL/SPI blend and its nanocomposite containing 5 wt % clay
4.2.3 RESULTS AND DISCUSSION

4.2.3.1 Morphology of the nanocomposites

X-ray diffraction (XRD) is generally employed to characterize the interlayer spacing in clay particles, which is correlated with their extent of intercalation. As the polymer chains are intercalated, the gallery height increases, resulting in shift of characteristic reflections to lower angles. If the complete exfoliation takes place, no peak would be seen in the X-ray diffraction pattern. Fig. 4.3-4.5 show the XRD patterns of the organoclay and the PCL/SPI/organoclay hybrids containing 1, 2.5 and 5 wt % organoclay, where the peaks correspond to the (001) plane reflections of the clay and the interlayer spacing calculated using Bragg’s equation is summarized in Table 4.1. It can be seen that the diffraction peak for the hybrids appears at a lower angle relative to that for the organoclay. Interlayer spacing of the organoclay is greatly expanded from 18.27 Å to 36.79 Å in the nanocomposite containing 2.5 wt % clay. This clearly indicates that the polymer chains are intercalated into the gallery of the organoclay during melt blending. The driving force for the intercalation of the polymer into the clay is believed to arise from the polar interactions between the polar groups present in PCL and SPI and hydroxyl groups existed in the organoclay (Cloisite 30B) used in this study (14). It is further observed that peak position of the hybrids is shifted to higher angle with the increase in clay content, implying adverse effect of the dispersion of the clay by increasing the amount of clay (15-17).

Dispersion of the clay layers in the polymer matrices can be confirmed in TEM photograph, as illustrated in Fig. 4.4. Nanometer-range intercalated clay tactoids are clearly shown in the figures. Dark lines correspond to the cross section of a clay sheet ca. 1 nm thick and the gap between the two adjacent clay lines is the interlayer spacing or gallery. For the nanocomposites containing 1 and 2.5 wt % clay (Fig. 4.4, 4.5), the organoclay particles consist of many single layers and thin multilayer stacks, which are uniformly dispersed in the matrix polymer. But, for the nanocomposites containing 5 wt % clay, multilayer stacks as well as agglomerated particles could be observed (Fig. 4.6).
4.2.3.2 Tensile and Dynamic Mechanical Properties

Figure 4.7 shows the effect of clay content on the Young’s modulus and tensile strength of nanocomposites. It can be seen that there is a great improvement in the Young’s modulus for the nanocomposites, and it increased with increasing clay content. For instance, the Young’s modulus is increased from 216 MPa for pure PCL/SPI blend to 359 MPa for the nanocomposite (66% increase) containing 5 wt % of the organoclay. The remarkable enhancement of the tensile modulus of the nanocomposites is due to tremendous interfacial interaction of clay nanoparticles with the polymer matrix. Immobilization of polymer chains induced by the large extent of intercalation of polymer chains between the silicate layers cause enhanced transfer of mechanical energy from the matrix to the high-modulus clay during deformation, and thus stiffness is increased.

There is a great improvement in tensile strength as well in the nanocomposites. The tensile strength of the nanocomposite with 2.5 wt % of clay nanoparticles is almost 50 % higher than that of the matrix. This is due to the substantial interaction between polar matrix and hydrophilic clay. The tensile strength of the nanocomposite containing 5 wt % clay is little smaller than that of the nanocomposite containing 2.5 wt % clay. Agglomerated particles formed by filler-filler interaction in the nanocomposite filled with 5 wt % clay, which was observed in TEM photograph, is supposed to cause the lowering of tensile strength. The filler agglomerates reduce interfacial area between filler and matrix polymer and acts as a stress concentrator and has detrimental effect on tensile strength of a material (18, 19).

The effect of clay content on the elongation at break of the nanocomposites is shown in Figure 4.8. The nanocomposites exhibited higher elongation-at-break as compared to the unfilled blend sample when the clay content is up to 2.5 wt %, which is supposed to due to the nanoparticle orientation and alignment during tensile deformation(20). This indicate a great enhancement in toughness in the nanocomposites as compared to unfilled PCL/SPI blend. But, the elongation -at-break of nanocomposite becomes lower when the clay content is increased to 5 wt %, which is due to the stress concentrating effect by agglomerated particles.

Effect of temperature on the reinforcing effect in the nanocomposites was investigated by means of dynamic mechanical analysis. Dynamic storage moduli of
PCL/SPI blend and its nanocomposites are shown in Figure 4.9. For all nanocomposites, the increase in the dynamic storage moduli of the matrix polymer over the investigated temperature range when compared to the neat polymer. The storage modulus at 30°C, for example, was enhanced from 520 MPa for unfilled blend to 680 MPa (30% increase) for the nanocomposites filled with 2.5 wt % clay. The remarkable enhancement of the storage modulus of the nanocomposite is due to the stiffening effect by the clay nanolayers. Restricted movement of the polymer chains in the nanocomposite enable the matrix polymer to sustain a high stress, which leads to the greatly enhanced modulus.

These observations indicate that, in the PCL/SPI/organoclay nanocomposite, the intercalation of polymer chains into the galleries of organoclay, even though each layer of the clay is not perfectly delaminated, can induce the effective enhancement in toughness and strength as well as stiffness.

4.2.3.3 Rheological Properties

Melt rheological behavior was analyzed to evaluate the processability of the nanocomposites. The elastic and loss shear modulus of the PCL/SPI blend and its nanocomposites containing 5 wt % clay are compared in Figure 4.10 and 4.11, respectively. The elastic shear modulus of the nanocomposites is higher up to frequency 1 rad/sec and above that frequency it is little lower than that of the unfilled sample. The terminal region slope of $G'$ and $G''$ of the PCL/SPI blend and its nanocomposites are shown in Table 4.2. It is observed that the slope of $G'$ and $G''$ of the nanocomposites are smaller than that of the unfilled sample. The higher $G'$ and smaller terminal slope of the nanocomposite over their unfilled counterpart indicates a formation of three dimensional superstructure in the nanocomposites. These results are also observed in other polymer-clay nanocomposites (7, 12, 21 and 22).

The frequency dependence of the complex viscosity of the PCL/SPI blend and its nanocomposite sample are shown in Figure 4.12. It is observed that at low frequency region complex viscosity of the nanocomposite is higher as compared to the PCL/SPI blend. This is due to strong interaction between the clay platelet and polymer in melted state. However at the high frequency region the complex viscosity of the nanocomposite is lower than unfilled PCL/SPI blend. This is due to the orientation of the clay nanoparticles in the high frequency region. The nanocomposite shows strong shear
thinning behaviour as the viscosity of the nanocomposite decreases with increased frequency. The shear thinning behavior of the PCL/SPI blend is only observed at high frequency. Thus PCL/SPI/clay nanocomposite has better processability compared to the pristine blend.

4.2.4 CONCLUSION

New eco-friendly, green nanocomposite from polycaprolactone/soy protein isolate blend and an organoclay by melt blending have been prepared. XRD and TEM study indicated that the polymer chains are intercalated into the gallery of the organoclay during melt blending. The nanocomposite showed great enhancement in toughness and strength as well as stiffness as compared to unfilled blend, even though each layer of the clay are not perfectly delaminated. The remarkable enhancement of the tensile and dynamic storage modulus of the nanocomposite was due to stiffening effect of the clay nanoparticles. The nanocomposites also showed strong shear thinning behavior which indicated excellent processability.
References


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