PREPARATION OF POLYPROPYLENE/POLYPROPYLENE GRAFTED CHITOSAN COMPOSITE

W. Onnongpong¹, P. Lertsutthiwong², K. Srikulkit¹,³*
¹ Department of Material Science, Chulalongkorn University, Bangkok, Thailand,
² The Metallurgy and Materials Science Research Institute (MMRI), Chulalongkorn University Bangkok, Thailand, ³National Center of Excellence for Petroleum,Petrochemicals and Advanced Materials,Chulalongkorn University, Bangkok, Thailand
*e-mail: kawee@sc.chula.ac.th

Keywords: chitosan, polypropylene-grafted-maleic anhydride, composite

Abstract: The polypropylene/ polypropylene grafted chitosan composite was prepared. In the first step, the modification of chitosan particle was achieved by reacting chitosan powder with maleated PP. In the next step, the obtained polypropylene grafted chitosan was mixed with PP resin using twin-screw extruder. The compatibility between polypropylene grafted chitosanand PP matrix was evaluated by optical microscope (OM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). Results are then discussed.

1 Introduction

Polypropylene (PP) is a thermoplastic polymer which is widely used such as packaging, automotive, and textile due to its excellent mechanical properties, low cost, low density and high water and chemical resistance. In addition, the incorporation of additives is generally carried out in order to enhance its properties. Natural fillers are one of candidates offering cost effective and renewable advantages. Chitosan is easy to prepare, biodegradability and non-toxicity. Due to the abundance of hydrophilic functional groups, chitosan is not melt when mixing with thermoplastic polymers. In order to solve this problem, some chemical modifications such as hexanoylation to introduce hydrophobic moiety to chitosan was studied. As a consequence, blending of PP with hydrophobic chitosan is possible.

The purpose of this study was to prepare PP/chitosan composite having the compatibility properties. Chitosan was prepared in the form of polypropylene-grafted-chitosan (PP-g-chitosan) prior to application. Polypropylene loaded with PP-g-chitosan was melt blended using twin screw extruder. The obtained PP/grafted chitosan composite was characterized by OM, SEM and TGA. The results were discussed.

2 Materials and Methods

2.1 Materials

Chitosan flak (Mw 52,000) was bought from AN LAB (AQUATIC NUTRITION LAB) and it was pulverized with a particle size of about 75μm prior to use. Tolune from italmar (THAILAND) CO,. Ltd, Isotactic polypropylene resin (Moplen® HP 561R) was from HMC Polymers Company Limited, Polypropylene-grafted-maleic anhydride from PI Industry Ltd. code ®Fusabond® P MZ109D Dupont with a melt flow rate of 120 g/10 min and heat stabilizer from Global Connections Public were used as received.

2.2 Methods

Modification of chitosan was carried out as follows: 100 g of PP–g-MA was dissolved in 1500 ml toluene at 85 ± 5 °C for 30 min. Then pulverized chitosan (20 g) was added. After stirring for 30 minutes toluene was removed by rotary evaporator. PP-g-chitosan in powder form was obtained. Then, the PP/PP-g-chitosan composite was prepared by twin screw operating at 200-225°C and 100 rpm/min using corotating mode. The composites loaded with 2%, 4%, 6%, 8% PP-g-chitosan were prepared.
2.3 Characterizations

Optical microscope (OM) was used to observe appearance. Scanning electron microscopy (SEM) was used to observe the morphology. TGA and DSC analysis was performed to study the thermal behavior.

3 Results and Discussion

The morphology of PP/PP-g-chitosan composite was observed by OM. Fig. 1 show the morphology of PP/PP-g-chitosan composite. As seen, the particle size of unmodified chitosan is very large due to its non-molten characteristic. In contrast, PP-g-chitosan particles are substantially smaller than unmodified chitosan particle, indicating that the modification of chitosan with PP-g-MA could further reduce the chitosan size. The small size of filler is desirable since it exhibits the good reinforcement effect and good compatibility with polymer matrix.

In addition, the morphology of PP/PP-g-chitosan composite was observed by SEM as shown in Fig. 2. As seen, PP-g-chitosan particles were scatter in PP matrix. However, agglomerates are observed, reflecting their poor compatibility with PP matrix. It is likely that these agglomerates of PP-g-chitosan particles represent those of chitosan particles having the incomplete modification.

Figure 2. SEM micrographs of PP/PP-g-chitosan composite: a (unmodified chitosan 1wt% -scale bar =5µm), b, c, d (2 wt%, 4 wt%, 6 wt%, 8 wt% PP-g-chitosan , respectively)
Fig. 3(a), 4(b), 5(c) show TGA thermograms of PP, chitosan and PP-g-chitosan, respectively. Fig. 3 shows TGA thermograms of PP/PP-g-chitosan composites containing 2%, 4%, 6%, 8% PP-g-chitosan. Fig. 3 shows that the degradation curves of the composites are indifferent to that of virgin PP. This indicates that PP-g-chitosan is highly compatible to PP matrix.

![Fig. 3(a) TGA thermogram of PP](image)

![Fig. 4(b) TGA thermogram of Chitosan](image)

![Fig. 5(c) TGA thermogram of PP-g-chitosan](image)

**Fig. 3. Thermogravimetric mass loss curves for PP and Chitosan**

**Table 1** decomposition of PP-g-chitosan and PP/PP-g-chitosan composites at various weight ratios analyzed by TGA

<table>
<thead>
<tr>
<th>Composite</th>
<th>First decomposition Onset temperature (°C)</th>
<th>Degradation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>442.5</td>
<td>441</td>
</tr>
<tr>
<td>unmodified chitosan</td>
<td>440.82</td>
<td>440</td>
</tr>
<tr>
<td>PP-g-chitosan 2%</td>
<td>439.62</td>
<td>455</td>
</tr>
<tr>
<td>PP-g-chitosan 4%</td>
<td>441.15</td>
<td>460</td>
</tr>
<tr>
<td>PP-g-chitosan 6%</td>
<td>440.59</td>
<td>458</td>
</tr>
<tr>
<td>PP-g-chitosan 8%</td>
<td>441.76</td>
<td>459</td>
</tr>
</tbody>
</table>

The table agreed that the decomposition of the composite of PP/PP-g-chitosan showed that all composites. The onset temperatures of thermal decomposition and decomposition temperature (Td) over poly propylene. It can be that the PP-g-chitosan can increase the thermal stability for poly propylene was. Because particles of substances both help induce the meat matrix crystals are more affected on the composite of PP/PP-g-chitosan have higher
crystallinity. The results will be seen that the PP-g-chitosan 4% decomposition temperatures due to the filler can be dispersed well enough in the polymer. Which when added to the filler too will the filler to hold the friendly causes Jai enough meat in the polymer was not good the decomposition temperature (Td) decreased.

Table 2 Melting temperature (Tm), crystallisation temperature (Tc), enthalpy of fusion(ΔHf) and percentage of crystallinity of various PP composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>Melting temperature (°C)</th>
<th>ΔHf (J/g)</th>
<th>% Crystallinity</th>
<th>Crystallisation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>162.9</td>
<td>62.74</td>
<td>30.1</td>
<td>113.3</td>
</tr>
<tr>
<td>unmodified chitosan</td>
<td>163.1</td>
<td>63.70</td>
<td>33.2</td>
<td>115.1</td>
</tr>
<tr>
<td>Chitosan 2%</td>
<td>164.2</td>
<td>73.03</td>
<td>35.8</td>
<td>118.9</td>
</tr>
<tr>
<td>Chitosan 4%</td>
<td>164.3</td>
<td>93.55</td>
<td>46.8</td>
<td>118.9</td>
</tr>
<tr>
<td>Chitosan 6%</td>
<td>164.4</td>
<td>82.61</td>
<td>42.2</td>
<td>120.2</td>
</tr>
<tr>
<td>Chitosan 8%</td>
<td>164.5</td>
<td>81.98</td>
<td>42.8</td>
<td>119.7</td>
</tr>
</tbody>
</table>

The thermal properties of various PP composites were investigated by using DSC technique as shown in table 2. The percentages of crystallinity of PP/PP-g-chitosan composite are higher than PP. This is due to the addition of foreign particles which favorably induce the crystallization of polypropylene matrix, leading to higher crystallinity of a polymer composite. However, the introduction of chitosan as well as PP-g-chitosan results in a slight increase in Tc since the average particle size of the filler is too big to induce the rate of PP crystallization.

4 Conclusions
PP-g-chitosan was successfully prepared. The loading of PP-g-chitosan into polypropylene was achieved by twin screw extruder. The OM micrograph showed that PP-g-chitosan particle was substantially smaller than that of unmodified chitosan. Due to its small size and hydrophobicity, PP-g-chitosan was well dispersed in PP matrix which was reflected by the TGA and DSC results that the degradation curve of PP/PP-g-chitosan was similar to that of virgin PP.

5 Acknowledgements
The authors gratefully acknowledge National Science and Technology Development Agency, National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, and Unisearch, Chulalongkorn University for financial support. Metallurgy and Materials Science Research Institute, Chulalongkorn University for laboratory support.

6 References
PREPARATION OF POLYPROPYLENE/POLYPROPYLENE GRAFTED CHITOSAN COMPOSITE