

In-situ Synthesis of Polyamide 6/POSS Nanocomposites

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS) plays an important role in the development of polymeric materials with improved properties due to their potential as candidate materials for bridging the gap between the organic polymers and inorganic ceramics [1]. Generally, the non-functionalized or functionalized POSS macromers were incorporated into the polymer matrix by blending or by chemical interaction, respectively. Due to the formation of amide linkage in the polymer chains, the use of amine functionalized POSS has a great deal in the development of hybrid materials with polyamide 6 (PA6). The synthesis of PA6/POSS nanocomposites was reported earlier by using aminopropyl-heptaisobutyl-POSS [2]. When compared with neat PA6, the marked decrease in the molecular weight was observed as a function of increase in the POSS loading and it was correlated to the chain terminating action of POSS-NH₂. However, the increase in molecular weight was observed by using previously synthesized heptaisobutyl-propylcarbamoylcaprolactam activator and appreciable increase in the mechanical properties of resultant polymer was also observed [3]. The nanocomposite of maleimide containing aromatic polyamide and amino functionalized POSS was also reported [4].

In the present investigation, the development of PA6/POSS nanocomposites with improved properties has been attempted by in-situ ring opening polymerization of ϵ -caprolactam with aminoethylaminopropylisobutyl-POSS (POSS AM0275, Figure 1) [5]. The synthesis was carried out by using 2.5 wt%, 5.0 wt% and 7.5 wt% of POSS AM0275 and the adipic acid was used to maintain the stoichiometric balance of amino groups in the reaction. The neat PA6 was also synthesized to assist characterization. An attempt was also made to improve the properties of PA6 without the need of activators and functional modifications. The resultant polymer nanocomposites were primarily characterized by Fourier transform infrared, differential scanning calorimetry and solution viscosity measurements. Further characterization will be carried out by ¹H NMR, X-ray diffraction, modulated DSC, and melt viscosity measurements.

Experimental

Materials. ϵ -caprolactam (CL) supplied by Kolon Chemicals Co. Ltd, Korea, aminoethylaminopropylisobutyl-POSS (POSS AM0275) from Hybrid Plastics, USA, adipic acid (AA) from Lancaster, 6-aminocaproic acid (ACA) and hexafluoroisopropanol, both from Aldrich chemical company, USA, tetrahydrofuran (THF) and formic acid, both from Samchun Chemical, Korea, were used as received. The double distilled water was used for product purification.

Polymerization. The polymerization process was carried out in an autoclave (Model R-201, Reaction Engineering, Korea) at atmospheric pressure. In the first step, the calculated quantities of CL, ACA as an initiator, POSS AM0275 and AA were introduced into the autoclave and the temperature was raised up to 100°C within 30 minutes time period. In order to ensure the adequate dispersion of POSS AM0275 and other additives in to the CL melt, the process was continued for another two and half hours with stirring (30 rpm) and nitrogen gas was purged continuously. In the second step, the temperature was raised to 230°C within 30 minutes and continued for another one and half hour to assist polycondensation. In the third step, the temperature was further raised to 260°C within 30 minutes and continued for another 4 h. In the step four, the vacuum was applied by previously attached vacuum pump to remove the unreacted substances. Finally the resultant polymer was extruded out in the form of spaghetti in an ice bath by purging nitrogen gas. The spaghetti were cut into small pieces to assist further purification and characterization.

Product Purification. The resultant polymer was purified by using two steps. In the first step, the unreacted CL, higher oligomers and other low mass species were removed by soxhlet extraction with double distilled water for 3 days and dried at 75°C under vacuum for 24 h. The unreacted POSS and other organic soluble species were

removed by soxhlet extraction with THF for 3 days and dried at 60°C under vacuum for 24 h.

Characterization. The above adequately purified products were primarily characterized by Bruker 66 V FT-IR, TA DSC Q 1000 and Schott AVS 260 auto viscometer. The resultant polymers were analyzed using FT-IR in the film form obtained by the solution casting on KBr window with hexafluoroisopropanol as a solvent. The DSC measurements were carried out with 10°C/minute scanning rate and -20°C to 250°C working temperature range. The solution viscosity measurements were carried out by using formic acid as solvent.

Results and Discussion.

The presence of Si-O stretching vibration peak at 1123 cm⁻¹ showed the presence of POSS AM0275 in the polymer [4]. The increase in the peak intensity was also observed as a function of increased POSS loading. In the case of neat POSS AM0275, the -NH stretching vibration peaks of primary and secondary amino groups overlapped at around 3422 cm⁻¹ and -NH bending vibration was observed at 1652 cm⁻¹. There was no significant variation in -NH stretching in the case of both neat and POSS loaded PA6.

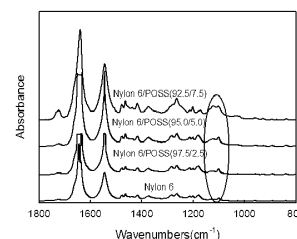
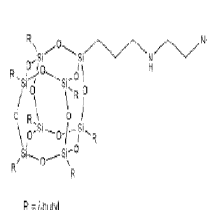


Figure 1. POSS AM0275

Figure 2. IR Spectrum of PA6/POSS

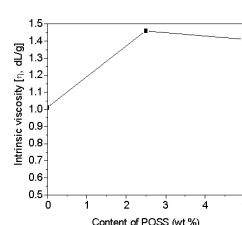


Figure 3. Viscosity analysis

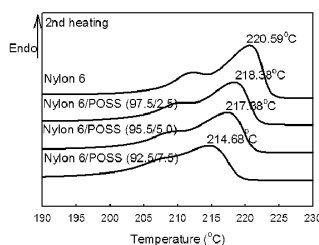


Figure 4. DSC analysis of PA6/POSS

DSC results showed the slight decrease in the melting point as a function of increased amount of POSS loading and it is associated with increased randomness due to the increased amount of POSS AM0275 copolymerized. The solution viscosity results showed the sharp increase in intrinsic viscosity up to 2.5 wt% and it remains nearly constant up to 7.5 wt%. The marked decrease in the solubility of 7.5 wt% PA6/POSS in formic acid as well as hexafluoroisopropanol was also observed and the proceedings of polymerization showed the increase in the torque value with respect to increase in POSS loading and better control needed to extrude the resultant polymer.

Conclusions

In-situ synthesis of PA6/POSS was effectively made by ring opening polymerization. The presence of Si-O stretching peak at 1123 cm⁻¹ with increase in intensity with increased POSS loading in IR spectrum, shifting of melting point to lower temperature regions in DSC analysis and marked increase in the values of intrinsic viscosity showed the presence and effect of POSS AM0275 in resultant polymer nanocomposites.

References

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