Rheological and Thermal Analysis of Polystyrene –Kaolin Nanocomposite Prepared By Solution Intercalation Technique

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Abstract

Polymer-clay nanocomposite of commercial polystyrene (PS) and kaolin were prepared via solution intercalation technique. Organically modified kaolin was used to render kaolin miscible with hydrophobic PS. Vinyl modified kaolin was used for the study. The kaolin was well dispersed in PS solution. Different amounts of nanoclay was added to polystyrene, to analyse the effect of nanoclay concentration in nanocomposite prepared. SEM analysis provides information of the morphology of the polystyrene-clay nanocomposite. Intercalation occurs at low modified clay content, whereas aggregation and aggregation occurs at high filler content. The thermal analysis and rheological analysis was carried on the PS-Kaolin nanocomposite. The results indicates the difference in property of polystyrene-nanoclay composite with filler loading.

1. Main text

Today, numerous researches are going on in the field of polymer engineering. Great emphasis is given to polymer-clay nanocomposite. A small amount of nanomaterial can alter the properties of the polymer material. The clay i.e. Fillers, in nano particle size exhibit properties different from normal sized clay particles. According to Xiaoan Fu et al. (2000), the dimension and microstructure of the dispersed phase significantly influence the properties of polymer composites. Polymer–clay nanocomposites have at least one ultra-fine dimension, typically on the order of 1 to 10 nm. As per Ansu Jacob et al. (2008), the fundamental principle of polymer clay nanocomposite formation is that the polymer should penetrate into the intergalleries of the clay i.e., the space between the platelets (layered galleries) of the silicate should be made accessible for the polymer chains.
Organic-inorganic composites have applications in many fields like electronics, automobiles, petroleum and mechanics. Polymer nanocomposite have attracted great interest, because they exhibit enhanced mechanical, thermal and barrier properties, according to J. Pinnavaia et al. (2000). As per Deviprasad Vanna P. R. et al. (2006), since PS is nonpolar, chemically inert, resistant to water and easy to fabricate, it is preferred for electronic, medical, food packaging, optical appliance and automotive applications. PS is one of the most investigated polymer because it is easy to polymerize and have a relatively linear structure.

Kaolin has wide range of application as filler in rubber, plastics, paper, and paint industries. L. Benco et al. (2001) shows Kaolin clay have 1:1 type layered structure: with one side of inter layer space is covered with hydroxyl groups of the Al(OH)$_4$ octahedral sheets and other side is covered by oxygen of SiO$_4$ tetrahedron and hence called 1:1 clay mineral. The nano sized kaolin clay can be obtained easily. Also on using the widely available kaolin clay the cost can be reduced significantly.

Solution intercalation is a simple and cost-effective way of preparing polymer-clay composite. This include separately dissolving the polymer and nanoclay in a common solvent. And then mixing the two solution, after which the solvent is made to evaporate by suitable method to obtain the nanocomposite. The solvent used in this study was Toluene.

The solution intercalation of polymer and silicate nanoclay may not form a nanocomposite. Nanoclay is naturally hydrophilic and polystyrene hydrophobic polymer. Also the clay layers are held tightly by electrostatic force according to Pankil Singla et al. (2012). This limits the use of nanoclay as such. If used as such the clay will not interact with polymer matrix. The nanoclay can be dispersed uniformly in the polymer matrix by modifying the nanoclay chemically with organophilic group. Here the vinyl modified kaolin nanoclay is used. The modification will increase the interlayer spacing of the clay. The good dispersion of nanoclay in the polymer matrix is verified by using the Scanning Electron Microscopy (SEM) images.

The work presented here tests the thermal and rheological properties of a polystyrene-kaolin (modified) nanocomposite prepared using solution intercalation technique. Modified kaolin concentrations are varied in each sample and all of them are compared.

2. Experimental

2.1 Materials

General grade polystyrene pellets are used as polymer. Toluene is the common solution used for dissolving both polymer and the filler. Kaolin nanoparticles which are vinyl modified are used as filler, this was obtained from English India Clay Ltd, Veli, Thiruvanantpuram. A mold made up of glass is used to pour the mixed solutions, to achieve a polymer sheet.

2.2 Preparation of PS–kaolin nanocomposites

The desired amount of Polystyrene, about 10gms is taken in a beaker containing 100ml of toluene. This is stirred using a magnetic stirrer for about 2 hours, after this a clear solution is obtained. Simultaneously in a separate beaker containing 50 ml toluene take 1% wt. (0.1gms) of vinyl modified kaolin nanoclay. Stir the same using magnetic stirrer for 1 hour. Now pour the modified kaolin nanoclay solution to the polystyrene solution. Mix the final solution well. Allow it to disperse well by placing it in a sonicator for about half-an-hour. Now this is transferred into a mould and kept in the open for the toluene to evaporate. After 2-3 days a polystyrene-kaolin nanocomposite sheet is obtained.

2.3 Equipment's

Scanning Electron Microscopy (SEM) images of the polystyrene kaolin nanocomposite samples and kaolin nanoparticles were obtained using a JSM-JEOL 6390 Scanning Electron Microscope. The JSM-6390 is a high
performance, low cost scanning electron microscope with a high resolution of 3nm. The customizable graphical user interface allows the instrument to be intuitively operated. It is equipped with an auto coater for coating the samples and the coating time is automatically adjusted by the coater and it varies according to the nature of the sample.

Thermal properties of the nanocomposite sample was studied using Thermo Gravimetric Analyser TGA - Perkin Elmer STA 6000. The sensor and proven compact furnace associated with this analyzer allows better temperature control, more consistent measurements and fastest cool down Time. Its operational temperature is from 15 °C to 1000°C. The samples were heated from 30°C to 800°C with 10°C/min increment.

Rheological properties were studied using Anton Par MCR 102 rheometer. This rheometer has Powerful, synchronous EC motor drive High-precision air bearing, including patented normal force sensor etc. The modularity of the system allows the integration of a wide range of temperature devices and application-specific accessories. The viscosity, amplitude sweep and frequency sweep were obtained using this rheometer.

3. Results And Discussion

We choose four samples of polystyrene and polystyrene-kaolin nanocomposite for the study. They are pure polystyrene, polystyrene intercalated with 1%, 2% and 5% wt. of vinyl modified nanoclay. The sheets are then used for testing in various machines. First the morphology of two samples were analysed followed by study of thermal and rheological property.

3.1 Characterization

The SEM analysis was done for the vinyl modified clay and the polystyrene intercalated with filler. The results are shown in Figure 1 and 2. Figure 1 shows that the vinyl modified clay was of extremely small dimension. Also the nanoclay was well dispersed in the polystyrene-clay nanocomposite.

![Fig. 1. SEM image of vinyl modified nanoclay](image1)

In Figure 2, the SEM image of polystyrene clay nanocomposite sample with 5% wt. of modified clay shows a good dispersion of the nanoclay.

![Fig. 2. SEM image of polystyrene clay nanocomposite sample with 5% wt. of modified clay](image2)
3.2 Thermal Properties

From the Figure 3, it is clear that degradation of all samples happen between 300 °C and 440 °C. The weight loss between these temperatures can be attributed to decomposition of organic compounds in clay interlayers.

![Comparison of Weight% v/s Temperature graphs of various samples.](image1)

The comparison of different samples shows that even though there is no significant change in thermal degradation temperature still the sample with 5% modified clay sample shows comparatively more thermal stability and its degradation temperature is little higher than others. The same sample’s residue remain even after 600 °C. The slight increase in degradation temperature may be due to the clay. Clay is an inorganic material, with good barrier properties and high thermal stability which can prevent the fast transmission of heat responsible for degradation.

3.3 Rheology

The graphs of viscosity v/s shear rate in Figure 4, shows that the viscosity decreases with increase in shear rate. This indicated that the fluid is a shear-thinning fluid.

![Comparison of viscosity v/s shear stress graphs of various samples.](image2)

The viscosity is highest for PS with 5% modified clay. The viscosity is due to the interaction between different layers of the material. As the interaction between the layers increases and becomes strong the viscosity increases i.e. the viscosity can be attributed to the strength of bonding between different layers of the material. Therefore, it is
clear that the strength is more for the PS with 5% modified clay.

4. Conclusions

The study covers the effect of kaolin nanoclay on the rheological and thermal behaviour of the polystyrene. Organically modified nanoclay was used for good adhesion with the polymer matrix. SEM analysis was performed and it revealed that the clay was of nano size. Also nanoclay was well dispersed in the polymer matrix. The thermal behaviour of the Polystyrene nanocomposite was studied for various concentration of added modified kaolin nanoclay. The sample added with 5% wt. of nanoclay showed more thermal stability than other samples, also the degradation happens at a higher temperature when compared with other samples. The rheological study of polystyrene nanocomposite indicates its shear thinning property. Decrease in viscosity with shear rate was shown by the nanocomposites. The highest viscosity was for sample added with 5% wt. kaolin nanoclay, which indicates that the stiffness of the material was increased. Stiffness of material is attributed to viscosity as viscosity is a measure of the interaction between different layers of polymer nanocomposite. Thus the addition of modified kaolin nanoclay has shown an improvement in the rheological and thermal properties of the polymer nanocomposite.

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References