

Preparation of Intercalated reactive groups through Sol-Gel modified-clay/polymer Nanocomposites

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Abstract: Tiethoxysilanepropylamineformylethyl trimethyl ammonium iodide (APS) and organic silane photoinitiator (1173IPS) was synthesized. The objective of this work is to intercalate reactive groups such as photoinitiator 1173IPS and epoxy into the montmorillonite (MMT) through Sol-Gel reaction of cationic triethyloxysilanepropylamineformylethyl trimethyl ammonium iodide (APS) and other trimethoxysilane with reactive groups. The modified clay was then mixed with resin to form oligomer-nanoclay composites by photopolymerization. XRD and TEM results showed that the modified-clay was exfoliated and dispersed parallelly as multilayer or monolayer in the organic matrix.

Keywords: montmorillonite; nanocomposites; photopolymerization; sol-gel; reactive organoclay; urethane acrylate;

1. Introduction

UV curable technology found considerable applications in micro and consumer electronics industries due to its rapid cure, solvent free characteristics, application versatility, low energy requirements and low temperature operation^[1-3]. Because of the advantages of UV curing, and the possibility of exceptional physical property enhancements of polymer-clay nanocomposite, such as stiffness, gas barrier, flammability retardance etc.^[4-8], in past decades, much research was focused on the UV curing polymer-clay nanocomposites^[9-15]. In order to build the chemical bonding between organoclay and polymer matrix, many kinds of ammonium surfactants and related onium ions with polymerizable reactive groups such as styryl group for polystyrene(PS)^[16], vinyl group for polymethyl methacrylate(PMMA)^[17] and rubber^[18], amine for epoxy resin^[19], were used to improved the affinity of montmorillonite toward organic materials.

To maximized the aforementioned properties, highly exfoliated clay dispersing in organic matrix are necessary. To obtain well intercalation and exfoliation, the critical is the ability to enhance intragallery polymerization rate catalytically to be comparable or greater than extragallery polymerization^[20]. In our previous work^[21] clay/polyurethane nanocomposites were prepared and the polymerization were induced by intercalated 1173TDI photoinitiator. Weimer^[22] reported preparation of PS/clay nanocomposite by situ living free radical polymerization using a silicate-anchored initiator. Alper Nese^[23] prepared clay/PMMA nanocomposites using intercalated phenacyl pyridinium salt

photoinitiators.

Almost all the modifiers were cationic ions or with cationic ions, then the modifiers could be intercalated into the intragallery through cationic exchange to copolymerize with organic matrix or initiate the polymerization. The aims of this paper were to intercalate reactive groups such as the methacrylate, the epoxy and the photoinitiator groups into the layered silicates through the Sol-Gel reaction of triethoxysilane propylamine formylethyl trimethyl ammonium iodide (APS) and trimethoxysilane with reactive group. The intercalated reactive groups not only enhanced the miscibility of organoclay with resin, but also built chemical bonding between clays and resin matrix after photopolymerization.

2. Experimental

2.1. Materials

CN 962 (urethane diacrylate oligomer) and 1,6-hexanediol diacrylate (HDDA) were donated by Sartomer Company. 2-hydroxy-2-methyl-1-phenylpropane-1-one (1173), was donated by ChangZhou Runtec Chemical Co.. Bis-phenol A based epoxy resin 828 from ChangXin Chemicals, china. 3-glycidoxypropyl trimethoxysilane (GPS) were donated by Jintan Hetou Organic Chemical Factory. APS and 1173IPS were synthesized in our laboratory. All reagents were used without further purification. The silicate used was sodium montmorillonite (Na-MMT) from Liufangzi Clay Factory, Jilin, China, with a cationic exchange capacity (CEC) of 78 mequiv./100 g.

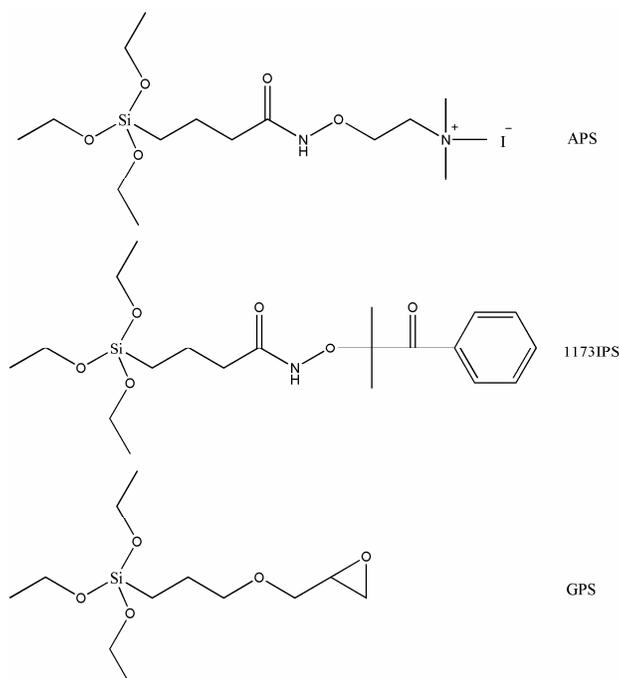


Figure 1. Structure of organic silanes with reactive group.

2.2. Preparation of organoclays

2.2.1. Modification of the Na-MMT

A mixture of 1.5g of 50% methanol solution of APS, 100mL of anhydrous ethanol, water and reactive silane such as GPS or 1173IPS were added into a 500mL single-necked flask equipped with magnetic stirrer and condenser. The mixture was stirred vigorously at 50°C for 24 h, and when 1173IPS was used, it should be in the dark to prevent any photolysis. The mass ratio of APS /1173IPS and APS /GPS were 1/1, 1/2, 1/3, 1/4, 1/5.

The clay mineral (1.5g) was dispersed in 100 mL of deionized water with magnetic stirrer for 2h at 50°C, followed by a 30min exposure in an ultrasound bath. Subsequently the clay mineral dispersion solution was added into above APS and solution in a few minutes, and the mixture was allowed to stand for 1 hour at 50°C. Then the mixture was centrifuged and redispersed in the mixture of deionized water and anhydrous ethanol (1/1, v/v). The process was repeated until no iodide was detected with 0.1N AgNO₃ solution. The modified clay was finally dried at 40°C for 24 h in vacuum oven. The 1173IPS modification process and mechanism was illustrated in Figure 2.

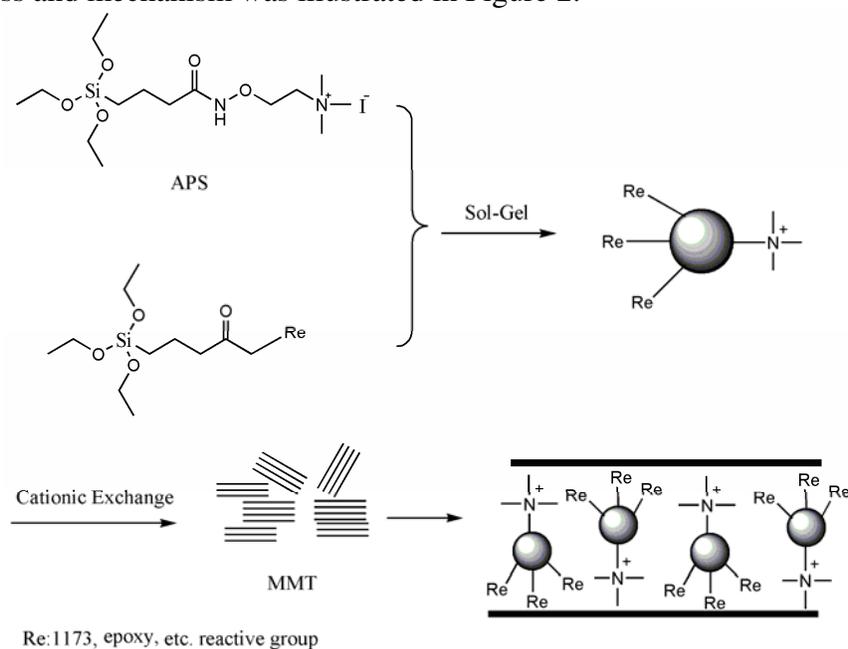


Figure 2. Schematic representation of clay modification.

2.2.2. Dispersion of organoclay in the photo-curing resins

The 1173IPS modified clay/resin nanocomposite resin formulation was typically the following: the mixture of CN 962 (70 wt%) and HDDA (30 wt%) was employed as the photopolymerizable resin and 5wt% of the different ratio of APS/1173IPS modified clay was used as the initiator and nanofiller.

As to the preparation of epoxy/clay nanocomposites, the process was as following: the modified clay (0.5g) was added to 10mL of acetone, sonicated to form a clay/acetone slurry. Afterward, the slurry was mixed with specific quantities of resin (828 from ChangXin Chemicals, china) as cationic polymerizable resin at 50°C and stirred for 2h. Acetone was subsequently allowed to evaporate at ambient conditions and then vacuum-dried at 40°C for 12h to remove remaining acetone (verified by

FTIR). Then 3% of a triarylsulfonium SbF_6 salt (6976 from ChangZhou Runtec Chemical Co.) as cationic-type photoinitiator was added, and the mixture was stirred and degassed under ultrasound.

3. Results and Discussion

3.1. X-ray diffraction of modified MMT.

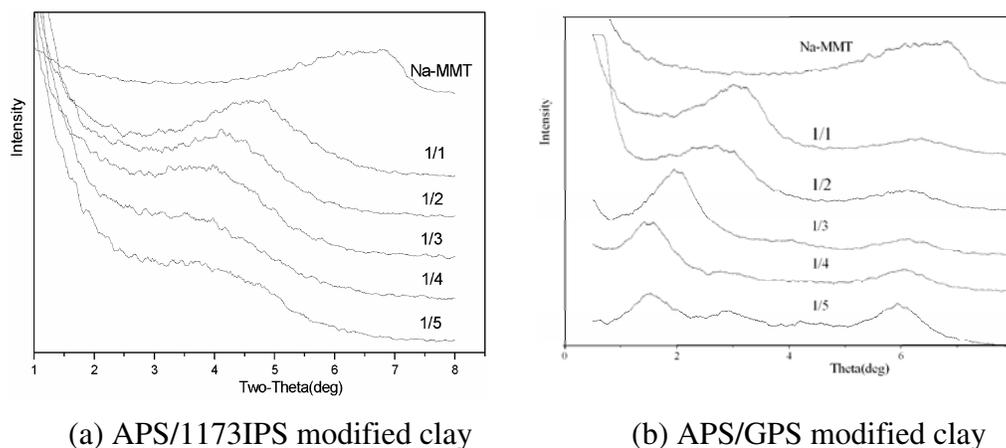


Figure 3. X-ray diffraction curves of Na-MMT, different APS/1173IPS modified MMT and different APS/GPS modified clay.

Table 1. The d -space of modified clay according to XRD

	d-space of modified clay	
	APS/1173IPS	APS/GPS
MMT	1.31nm	1.31nm
1/1	1.94nm	2.9 nm
1/2	2.05 nm	3.2 nm
1/3	2.12 nm	4.4 nm
1/4	2.26 - 3.65 nm	5.9 nm
1/5	2.28 - 3.71 nm	5.7 nm

The hydrophobic behavior and an increase in d spacing between the layers of silicate are important factors which make organophilic montmorillonite compatible with most hydrophobic polymers, so the d spacing of the organoclay was studied by X-ray diffractometer, and the d spacing were listed in Table 1. After 24h Sol-Gel reaction, APS reacted with 1173IPS, forming dimer, trimer tetramer or oligomer of APS and 1173IPS which had ammonium head group and 1173 reactive groups. The X-ray diffraction curves of modified organoclay of different ratio of APS/1173IPS and APS/GPS were presented in Figure 3. The 1/1 ratio modified clay showed a diffraction peak at $2\delta = 4.6^\circ$ as opposed to the diffraction peak at $2\delta = 6.8^\circ$ for the unmodified montmorillonite, which showed that APS have intercalated into silicate layers, and enlarged the d spacing from 1.31nm to 1.94nm. When the amount of 1173IPS increased, the

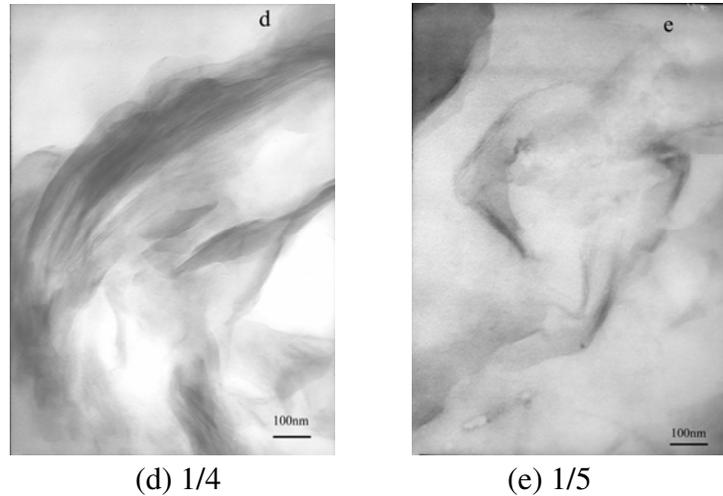
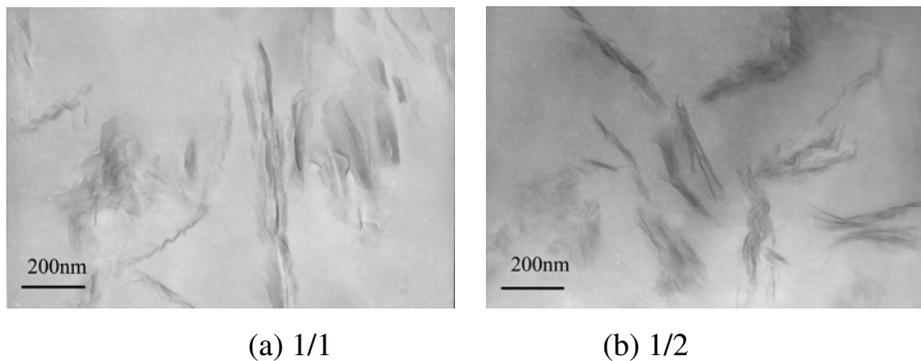


Figure 4. Morphology of the polyurethane-clay nanocomposite containing 5 wt% of organoclay modified with different ratio of APS/1173IPS.

In the APS/GPS=1/1 modified clay-epoxy nanocomposites, large particles existed. In Figure 4(b), primary particles consisting of groupings of parallel layers with large dimensions from 30 to 100nm existed in the APS/GPS=1/2 modified clay-epoxy composites. The space between silicate layers appeared to range from 20 to 40 nm, which is larger than the original 1.4 nm space between silicate layers in organoclay. This is direct evidence that these silicate layers have been exfoliated and a nanocomposite of orderly exfoliated silicate layers and epoxy resin has been prepared.

When the ratio of APS to GPS increased to 1/3, the silicate was much smaller than that of the 1/2 ratio of APS to GPS modified clay-epoxy nanocomposites, and the clay were highly exfoliatedly dispersed in epoxy matrix, as displayed in Figure 5(c). For the 1/4 and 1/5 ratio of APS to GPS modified clay-epoxy nanocomposites, the organoclay was uniformly dispersed in epoxy resin, and highly exfoliated. The silicate layers were found to be not only exfoliated but also disorderly dispersed at the monolayer level.



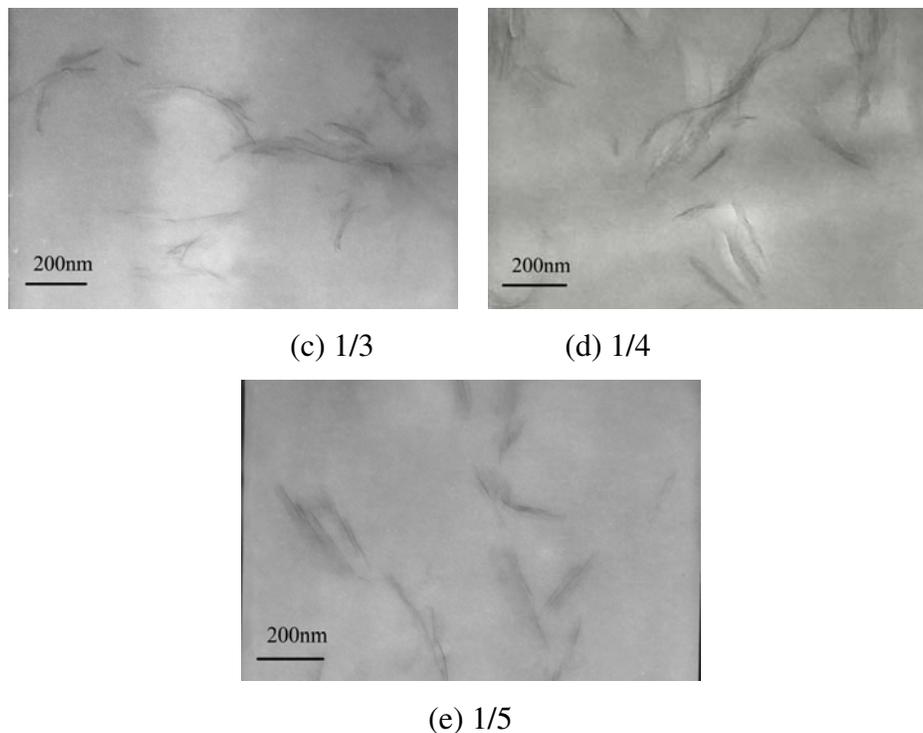


Figure 5. Morphology of the epoxy-clay nanocomposite containing 5 wt% of organoclay modified with different ratio of APS/GPS.

4. Conclusions

This study developed a new and convenient method to prepare functionalized organoclay by Sol-Gel reaction of triethoxysilanepropylamineformylethyl trimethyl ammonium iodide (APS) and reactive group silane such as GPS, 1173IPS. The reactive groups were intercalated into the layered silicates with the ammonium head groups through the cationic exchange. The mass ratio played a very important role on the enlargement of d spacing and the morphologies.

This approach provided a novel pathway for the highly exfoliated clay-polymer composites designing intercalating agents capable of introducing different functional groups such as (meth)acrylate, epoxy, amine etc. into the layered silicates.

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