Functionalization of Montmorillonite and Possibilities of Synthesizing a Urethane Oligomer on the Surface of Nanoparticles

Oleksii Gonchar, Yuri Savelyev

Institute of macromolecular Chemistry, NAS of Ukraine, Kharkovskoe shosse, 48, 02160 Kyiv, Ukraine, E-mail: <u>lexgon@ukr.net</u>

Abstract

In order to create an organoclay with a surface functionalized with amino groups, a method of modifying montmorillonite with a cationic oligourethane with available amino groups was developed. On the surface of the functionalized nanoparticles reactions of sequential addition of monomers were carried out.

Keywords- montmorillonite, modification, modifier, organoclay, cationic oligourethane.

Introduction

Imparting the surface of silicate nanoparticles the organophilic nature is an urgent problem for the production of polymer organo/inorganic nanocomposites with montmorillonite (Mt) and other layered silicates. Surface modification of Mt nanoparticles has been widely used in recent years due to their use in the production of organoclay nanocomposites [1]. These nanocomposites possess an increased mechanical strength compared to the mother polymers. Modification of the nanoparticles surface of layered silicate using some organic surfactants is necessary to increase a compatibility between the polymer and clay [2]. Better compatibility between matrix and excipient can result in enhanced physical properties. Common modifiers used for the organic modification of Mt are cations of organic quaternary ammonium salts [3, 4], cations of quaternary phosphonium salts [5, 6], diamines [7] and amino acids [8]. Mt modified with organic cations is dispersed in a polymer matrix, where it acts as a reinforcing agent improving the properties of polymer material. Sometimes, conventional alkylammonium cations are not suitable for the Mt modification. In the case of polar polymers, such as polyurethanes, polyamides, polyepoxides, Mt modified with aliphatic surfactants does not lead to exfoliation in the polymer matrix. This is due to the lack of a sufficiently high-quality interaction between the nanofiller and the polar polymer matrix [9, 10, 11]. In case of non-polar polymers (polyethylene, polypropylene, etc.), Mt modified with aliphatic surfactants is easily exfoliated in a polymer matrix [12]. This is explained not only by the non-polar nature of the modifier, but also by the high interlayer distance of the modified Mt. High interlayer distance is provided by sufficiently large hydrocarbon moieties of the organic modifier. At the same time, the molecules of polar monomers used in polycondensation reactions do not have large sizes for expansion of Mt layers sufficient for exfoliation [13]. Thus, it can be concluded that to create nanocomposites based on polar polymers it is important to use modifiers comprising sufficiently large fragments to increase the interplanar spacing, as well as polar fragments to increase the affinity for the polar polymer. The authors of this work previously synthesized cationic oligourethanes having two sufficiently large fragments of 17 to 21 atoms length and having a polar urethane nature [14]. In this work, oligouretane amonium chloride (OUAC) was synthesized based on N-methyldiethanol amine (NMDEA), 1,6-hexamethylene diisocyanate (HMDI), and isopropyl alcohol. This cationic oligourethane has two polar fragments with a length of 17 atoms, which provides an increase in interplanar spacing and allows the modified Mt to delaminate in an environment of polar organic

solvents. In addition, such a modifier provides high affinity for the polar polymer, forming nanocomposites with fully exfoliated Mt, which increases the strength of the polyurethane material by an average of 40%. This work is a logical continuation of the previously obtained results. However, the new modifier oligourethane amine ammonium chloride (OUAAC) with terminal aminogroups which was synthesized on the basis of NMDEA and HMDI revealed completely new possibilities in the field of organoclays and organo/inorganic nanocomposites creation. Namely, the ability to carry out stepwise synthesis on the surface of modified Mt nanoparticles by the mechanisms of both polyaddition and polycondensation. This work gives a few examples of such synthesis with the use of aliphatic and aromatic diisocyanate, as well as an example of the sequential addition of aromatic diisocyanate, glycerol and repetitively aromatic diisocyanate.

Results and discussion

A two-stage, simple and at the same time efficient synthesis of cationic oligourethane OUAAC was developed. A characteristic feature of the synthesis of the modifier is the appearance of functional amino groups, occurring simultaneously with the formation of tertiary ammonium cation and the formation of OUAAC solution of a given concentration. That is, as a result of such an unique and simple process, a target product appears in the form of a modifier solution of a given concentration, which is ready to be added to the aqueous dispersion of Na-Mt. No by-products are formed, provided the exact proportions of reagents.

Synthesis on the nanoparticles surface of modified with OUAA/Mt was carried out in DMF. The dispersion of OUAA/Mt in DMF was obtained by sonication (with cooling) for 30 minutes of a mixture of modified Mt with DMF with content of OUAA/Mt (1 - 1.5)%. Diisocyanates were added to the obtained OUAA/Mt dispersion in DMF, and after sonication for 30 min, it was left for a day at 60 °C. All processes took place in an inert gas environment. After that, the dispersion was centrifuged, washed twice and centrifuged to completely clear from diisocyanate.So, to obtain a modified Mt functionalized with HMDI, OUAA/Mt was treated with a four-fold excess of HMDI. After 30 min of sonication of the dispersion mixture of OUAA/Mt and HMDI, some sedimentation of the modified Mt in DMF and the formation of a bulk suspension were observed. After holding for f day at 60 °C, the resulting dispersion was centrifuged many times and washed with DMF. The functionalization of OUAA/Mt by aromatic DFMDI was carried out similarly. Thermogravimetric analysis of functionalized by HMDI OUAA/Mt showed an increase of the organic component up to 32% wt. This value corresponds to the addition of HMDI to all amino groups of modifier. However, thermogravimetric analysis of the functionalized by DPMDI OUAA/Mt showed an organic component content of 46% wt. In order to study the possibility of stepwise synthesis on the nanoparticles surface of OUAA/Mt, the sequential addition of DPMDI, glycerol and again DFMDI was carried out. The previously obtained gel of functionalized by DPMDI OUAA/Mt in DMF was treated with a four-fold excess of glycerol using ultrasound in an inert gas atmosphere, for 30 minutes. The resulting mixture was further kept at 50 °C for 24 hours. The product obtained after reaction with glycerin was repeatedly centrifuged and washed with DMF. The gel of organically modified Mt in DMF, purified from glycerol residues, was treated with a four-fold excess of DPMDI as described previously. Thermogravimetric analysis of the product obtained after three-step synthesis on the OUAA/Mt nanoparticles surface, showed an organic matter content of 56% wt. This organic content corresponds to the amount of attached DPMDI.

Conclusions

The developed scheme for the synthesis of cationic oligourethane amine ammonium chloride, which results in a prepared modifier solution with a given concentration ready for montmorillonite modification, is distinguished by its simplicity and effectiveness.

It has been experimentally proofed that montmorillonite modified with oligourethane amine ammonium chloride has an accessible for addition reactions amino groups on the nanoparticles surface.

The synthesis on the nanoparticles surface of modified with oligourethane amine ammonium chloride montmorillonite in a polar solvent medium allows both functionalizing the organically modified mineral and increasing organophilicity and interplanar spacing.

The possibility of synthesis of regular structure oligomer on the nanoparticles surface has been shown by the example of stepwise diisocyanates addition; it can be used for matrix synthesis on montmorillonite nanoparticles.

Montmorillonite modified with oligourethane amine ammonium chloride offers great opportunities for the design of the organic layer on the nanoparticles surface using both diisocyanates and other functional compounds, such as anhydrides and others.

The use of montmorillonite with a reactive surface opens up enormous opportunities in the field of creation of hybrid organo/inorganic nanocomposites based on polar polymers.

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