



The effect of covalently modification of montmorillonite by 3-glycidoxy propyl trimethoxysilane on its dispersibility in TPU/MMT nanocomposite

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Abstract

In this work, the silylation of sodium montmorillonite (Na^+ -MMt) was performed using (3-Glycidoxypropyl)trimethoxy silane (GPTMS). Different amount of the silane were used to modify clay surface. Thermoplastic polyurethane (TPU)/clay nanocomposites were produced by incorporation of 3wt % loading organically modified montmorillonite clay (SMMT) in TPU matrix by melt-mixing route. The grafting/intercalation of the GPTMS inside the Na^+ -Mt interlayer spaces was studied by means of thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR). Thermoplastic polyurethane (TPU)/clay nanocomposites were analyzed by means of Low angle X-ray diffraction (XRD). The results showed that silane grafting improved the nanoclay dispersibility in TPU matrix, possibly due to the improved interaction between the hydrophilic mineral platelets of clay and TPU chains. The best result was found for SMMT2.

Keywords: organic nanoclay, silylation, TPU, nanocomposites,.

Introduction

Polyurethanes are extraordinary and versatile polymeric materials that have exceptional properties such as excellent flexibility, elasticity, wide range of hardness, good shear strength, good abrasion resistance, good chemical strength. because of its textile properties, it is widely used in coatings, adhesives, sealants, foams, fibers, films and more [1]. Polyurethanes are widely used in the aerospace industry, packaging industries, automotive industries and medical applications [1,2].

However, most polymer films, unlike polyurethane, are in the low degree with properties such as low temperature flexibility, weathering resistance, tensile fatigue and adhesion. However, these films have lower inhibitory properties than other polymer films [3]. Despite their diverse properties, the major drawback of polyurethanes is their inherent permeability to gases and vapors, including oxygen, nitrogen, carbon dioxide and helium, water and organic vapors.

Improving the barrier properties is important in areas where your polyurethane is used as a film, membrane or coating [4].

Much research has been done to improve their gas barrier properties chemical modification of polyurethane or changing its morphology, by appropriate selection of components,



composition and preparation conditions. However, these methods do not have a significant effect on the improvement of barrier properties [5,6].

In recent years extensive research has been devoted to organically modified clay as reinforcements for polymers. Their layered morphology, high aspect ratio and the nanoscopic phase distribution lead to improved thermal, mechanical, and gas barrier properties. The gas barrier properties in polyurethane membranes is dramatically increased by the addition of layered silicates. These materials mainly impede gas diffusion physically. They resulting in a tortuous and longer the gas diffusion path, as a result it enhances barrier properties of nanocomposite [4].

It is important to modify the clay nanolayers. In this regard, numerous studies have been carried out to modify the surface of the Na⁺-Mt, in particular, modifying with surfactants (such as alkyl ammonium salts) via a cation exchange [7]. However, these surfactants only have an electrostatic interaction with clay nanosheets, which can be eliminated during the process of polymers under high process temperatures. Therefore Chemical modification methods, which mainly involve the binding of an organic molecule, have been considered due to their higher chemical and thermal stability [8].

Chemical modification is generally carried out with silane coupling agent. In this modification, silanols (Si-OH) react with hydroxyl groups on the surface of Na⁺-Mt layers and introduce specific functional group to polymer matrix, ideally it can form a network between the clay, silane and polymer matrix layers and greatly enhance the properties of the composite [9]. A schematic representation of the layered silicate clay structure and the silylation reaction are shown in Fig.1.

These organically modified clays increase the compatibility of the clay platelets with the polymers, allow the polymer chains to enter the layer by increasing the spacing of the layers and to achieve exfoliated dispersion [10].

In this study, we modified montmorillonite (Na-MMt) by grafting using 3(Glycidoxypropyl)trimethoxy silane (GPTMS) , and the nanocomposites with TPU were prepared by melt blending. Different characterization techniques, such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and Xray diffraction (XRD) were used to investigate the grafting process and clay dispersion.

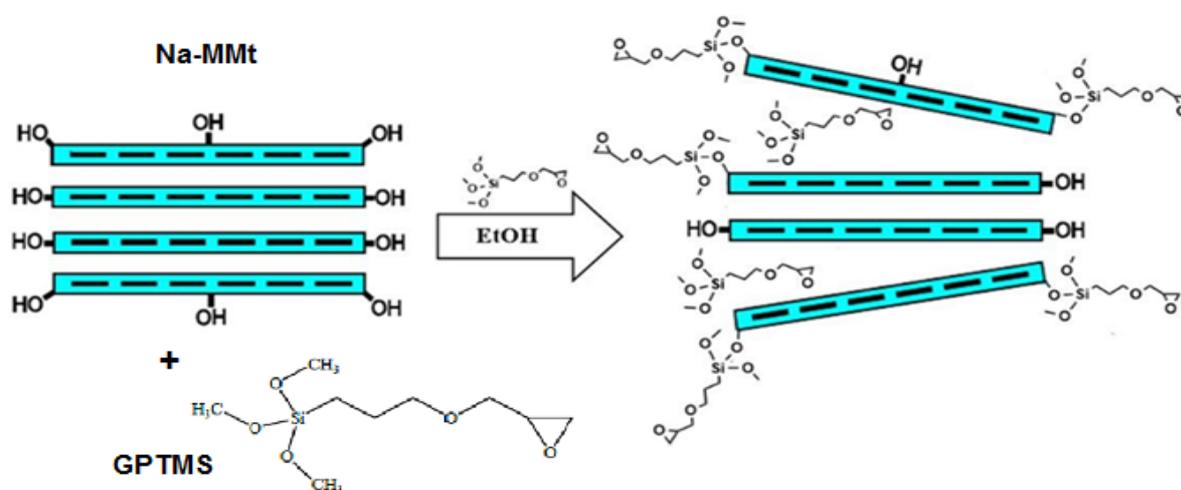


Fig.1. Schematic representation of grafting of GPTMS onto the clay platelets.



Experimental

Materials

Pristine montmorillonite (Na-MMT) was purchased from UK florachem. 3-glycidioxypropyltriethoxymethoxysilane silane (GPTMS) was obtained from Sigma Aldrich. polyester-based thermoplastic Polyurethane with the trade name coim 9025 was supplied. Acetone and Ethanol is used as a solvent and acetic acid to adjust the pH of the solution.

Functionalization of Na-Mt

The silylation of the pristine clay was performed by dispersing 3 g of dry Na-MMT in 150 mL of ethanol and was sonicated in water bath for 30 minutes at room temperature. The pH of the suspension was adjusted by acetic acid to about 4. Acid facilitates hydrolysis and formation of silanol groups by silane molecules and accelerates the condensation reaction of these groups with the hydroxyl groups of the clay surface. GPTMS with weight ratios of 1, 2 and 3 to Na⁺-MMt were selected for surface modification and respectively named: (SMMT1), (SMMt2), (SMMt3). GPTMS was dissolved in ethanol and dropwise added to the suspension. The mixture was heated at 80 °C for 24 h. The resulting suspension was filtered using Buchner funnel and washed three times with ethanol and washed with methanol. Finally, the resulting powder was placed in an oven at 70 °C for 24 hours.

Preparation of TPU-clay nanocomposites

The required amount of polyurethane and SMMt were dried for 2 h at 60 C to remove moisture. The dried SMMt was sonicated in small amount of acetone to separate out the clay-layers to some extent and TPU granules were mixed with it. Subsequently, the clay-coated polyurethane granules were dried properly in oven to remove acetone and residual moisture. Then, It was processed in the micro twin-screw brabender (83b201/012 OHG Duisburg, Germany) under the process conditions: Temperature=185 C, screw-speed=60 rpm, and residence time=13 min.

Characterization

FTIR spectroscopy was carried out using a AVATAR FTIR spectrometer in transmittance mode. A very small amount of modified clay was mixed with KBr powder and was pressed into a disk, which was then placed inside the FTIR chamber to obtain the spectrum. The test was carried out within the range of 4000–400 cm⁻¹.

Low angle X-ray diffraction (XRD) studies were performed on a X'Pert MPD Model from Philips Analytical X-ray diffractometer (Netherland) (CuK α irradiation, 40 kV, 30 mA) in the range of 2 θ =2–10°. Low Angle-XRD, was used to investigate the d-spacing and the state of exfoliation of silicate platelets in the polyurethane thermoplastic matrix.

A thermogravimetric analyzer (TA instruments – Q600, New Castle, USA) was applied to determine the amount of grafted silane on Na-Mt, and to study the thermal behavior of the modified clay. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under argon flow.

TGA results can provide

qualitative and quantitative insight into the approximate amounts of intercalation, and chemically grafted silane onto clay platelets. The grafted amount was evaluated using Eq. (1) from the mass loss between 200 °C and 600 °C [7].

$$\text{Grafted amount} \left(\frac{\text{mmol}}{\text{g clay}} \right) = \frac{\Delta w_{200-600} \times 1000}{w_{600} \times M} \quad (1)$$



Results and discussion

Clay characterization

In order to verify that the layered sodium montmorillonite was successfully modified with (3-glycidyloxypropyl) trimethoxysilane and to fully characterize the starting material, the functionalized clay SMMT was submitted to TGA and FT-IR analyses.

TGA

Thermogravimetric analysis (TGA) was performed on Na-Mt powders before and after the silylation process Fig.2. It is obvious that the mass loss of the silane-modified clay (SMMT1) is greater than that of pristine Na-Mt, indicating that GPTMS was successfully grafted onto Na-Mt. From TGA analysis, the mass loss between 200 °C and 600 °C was input into Eqs. (1) to estimate the amount of grafted aminosilane.

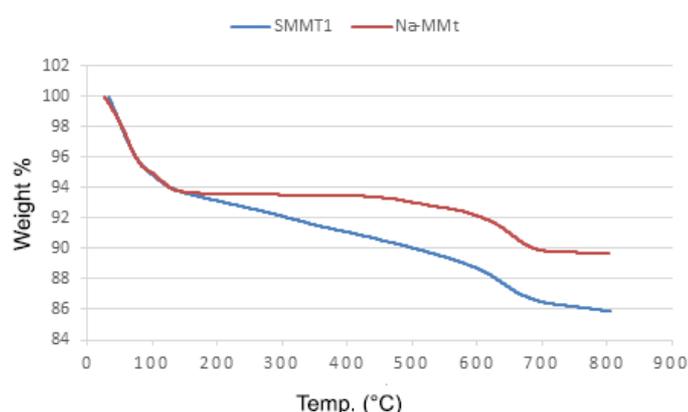


Fig.2. TGA degradation patterns of untreated Na-Mt and silane-modified Na-Mt (SMMT1)

Table.1. Mass loss and silane grafted amount of the modified samples

sample	Mass loss (gr)	Mass loss (%)	Grafting amount (mmol)
Na-MMT	0.4647	10.35	-
SMMT1	0.7205	14.13	0.2117

FTIR

The FT-IR measurements confirm the organosilylation of the original clay. The FTIR spectra of pure Na-MMT and the clay modified with GPTMS (SMMT1, SMMT2 and SMMT3) compared in Fig.3. The strong peak at 1038 cm⁻¹, attributed the stretching of Si-O groups. All the spectra are characterized by -OH transmission bands at 3627 cm⁻¹, due to stretching vibrations of Al-OH and Si-OH, and at 3413 cm⁻¹ and 1638 cm⁻¹, due to stretching and bending vibrations of the interlayer water [11]. A decrease of the intensity of the peak at 3627 cm⁻¹ (Fig.3.a) (corresponding to the stretching vibration of the hydroxyl groups) was observed in the spectrum of the modified clay, indicating that some modification actually took place. The silylation of the pristine clay was also confirmed by the presence of a weak and broad band at 3000-2800 cm⁻¹ (Fig.3.b), attributed to the stretching vibration of the methyl



and methylene groups introduced by the organic modifier. With the increase in the amount of silane from the SMMT1 to the SMMT3, these peaks also increased. The bands at 529 cm⁻¹ and 470cm⁻¹ (Fig.3.c) related to the bending vibration of Si–O–Si and Si–O–Al showed increased intensity for the SMMTs and these observations suggest the successful grafting of the silane on the surface of the clay [12].

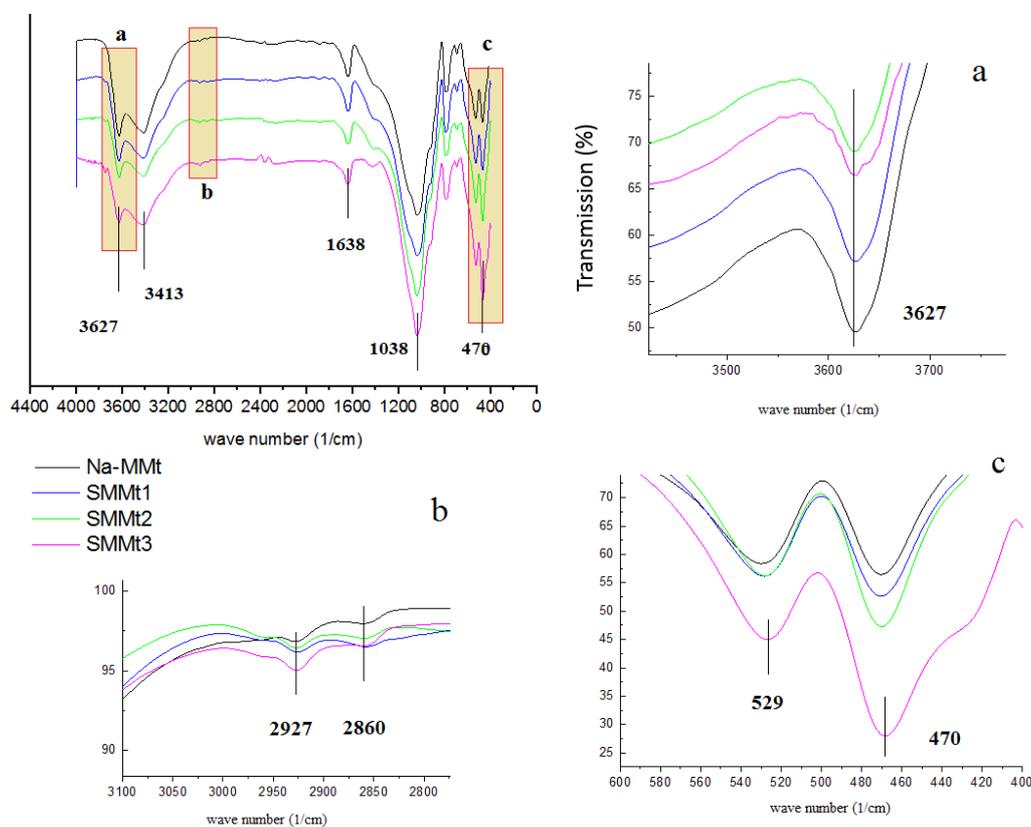


Fig.3. FT-IR diffractograms for the pristine MMT and the SMMTs after treatment

TPU/clay nanocomposite

Low angle X-ray diffraction analysis (XRD)

The Low angle X-ray diffraction analysis is used to identify the dispersion state of nanoparticles in the polymer matrix. The X-ray diffractograms for the neat TPU and TPU nanocomposites are displayed in Fig.4. The TPU is amorphous, as expected and indicated by a broad amorphous halo. A decrease in the peak intensity followed by a decrease in the diffraction value, indicated the better clay platelets dispersion. The graph clearly shows that the original peak of SMMT2 is almost absent in the diffraction patterns of the TPU/SMMT2, demonstrating that the clay is dispersed on a nanometric scale nearly exfoliated in TPU matrix. However, the other modified samples (TPU/SMMT1, TPU/SMMT3) the peak was not eliminated but the intensity of the peak was decreased compared to the unmodified nanocomposite (TPU/Na-MMT). Peak reduction in the modified samples confirmed improvement of clay miscibility in TPU compared to the pristine Na-MMt.

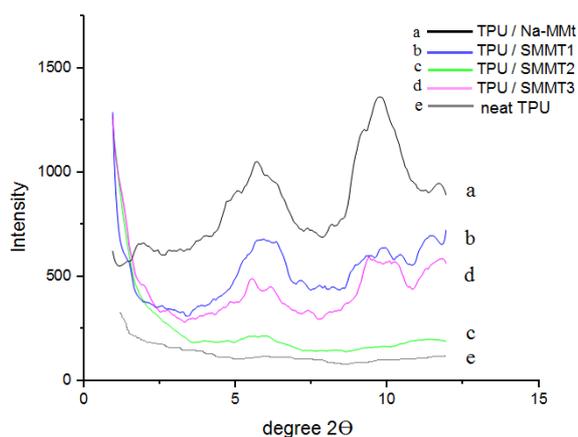


Fig.4. X-ray diffractograms for the pristine MMT and the MMT after treatment

Conclusions

A study was performed on the silylation process of Na-Mt in order to obtain the optimum concentration of silane for synthesizing more compatible modified Na-Mt with TPU matrix. An organically modified MMTs were first successfully prepared by a subsequent grafting using silane coupling agent (GPTMS). The FTIR and The TGA analysis confirmed that GPTMS molecules have been grafted on the MMT surfaces. The amount of chemical grafting were estimated based on TGA data via equation. The role of silane concentration in the interlayer space were characterized.

Nanocomposites were produced by incorporation of 3wt% loading organically modified montmorillonite clay (SMMT) in TPU matrix by melt-mixing route. The organically modified MMT in the TPU matrix were demonstrated using XRD. The results showed that silane grafting improved the nanoclay dispersion in TPU matrix, possibly due to the improved interaction between the hydrophilic mineral platelets of clay and TPU chains. The best result was found for SMMT2. As the amount of silane increases, the locking effect may occur and the silane molecules condense together at the edges, and results in aggregation.

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