

研究简报

用于制备聚氨酯纳米复合物的高岭石粒子的表征

李再峰^{*·1} 王义银² Luba S. Kotlyar³ Keng H. Chung⁴⁽¹⁾ 青岛科技大学化学与分子工程学院, 青岛 266042)⁽²⁾ 西安交通大学管理学院, 西安 710049)⁽³⁾ ICPET, National Research Council, 1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6)⁽⁴⁾ Syncrude Canada Ltd., Edmonton Research Centre, 9421-17th Avenue, Edmonton, Alberta, Canada, T6N 1H4)

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Characterization of Nano Kaolinite Clay used in Polyurethane Composite

LI Zai-Feng^{*·1} WANG Yi-Yin² Luba S. Kotlyar³ Keng H. Chung⁴⁽¹⁾ School of Chemistry and Molecule Engineering, Qingdao University of Science and Technology, Qingdao 266042)⁽²⁾ School of Management, Xi'an Jiaotong University, Xi'an 710049)⁽³⁾ ICPET, National Research Council, Montreal Road, Ottawa, Ontario, Canada K1A 0R6)⁽⁴⁾ Syncrude Canada Ltd., Edmonton Research Centre, 9421-17th Avenue, Edmonton, Alberta, Canada, T6N 1H4)

Clay such as kaolinite, is commonly used as an additive to modify the thermal properties of polymer. In this paper, the morphology, composition, shape and structure of kaolinite was characterized by various advanced techniques. The TEM/EDX data showed that the kaolinite had a larger particle size and a Si/Al ratio of 1.8. The individual particle of kaolinite was a single crystalline. TEM also showed that these particles were always stacked together due to the presence of electrostatic cohesive energy and hydrogen bond between plaletes. The PAS-FTIR spectra showed that no absorbance of hydroxyl group for hydration water in hydrogen bond region or at 1650cm⁻¹ was observed at room temperature. It meant a little ability to adsorb water for kaolinite particle. Kaolinite clay also showed no change for its PAS-FTIR spectra with increasing temperature. The TGA results revealed that kaolinite almost doesn't lose weight at 60°C due to loss of dehydration of absorbed water, however, it will decomposed around 510°C and lose its hydroxyl functional group in the form of water (dehydroxylation). The result is consistent with that of PAS-FTIR analysis. This suggests that the structural hydroxyl group on the surface of individual kaolinite clay particle is very stable below 500°C, and the kaolinite composed polymer could be got by the reaction of its stable structural hydroxyl group with isocyanate group of polyurethane prepolymer.

Keywords: kaolinite clay characterization nano composite polymer

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* 通讯联系人。E-mail: 970129@public.qd.sd.cn

第一作者: 李再峰, 男, 36 岁, 副教授; 研究方向: 材料化学和环境工程。

0 Introduction

Polyurethane(PU) is a versatile polymeric material, which can meet the diversified demands of modern technology, and was used in wide range of application as coating, adhesives, thermoplastics elastomeric material, foams, etc. In our previous works, the kinetics, morphology change during its bulk polymerization process, structure and morphology, relationship between properties and their structure, were investigated in detail^[1-5]. However, The thermal properties of PU was not satisfied to us, its mechanical properties were decreased much above 70°C^[2]. In order to improve its shortcomings, while keeping its superior mechanical properties at room temperature. Much work has been done by dispersing inorganic or organic fillers in polyurethane polymer. A wide variety of additives, i. g mica, wollastonite, etc. has been employed in PU formation^[6]. Unfortunately, these additives often resulted in a reduction in the elongation at break. It was well known that many kinds of clays have kinds of hydroxyl group on their surface, strong interaction between the clay and polar groups, such as urethane group and urea link, should be present. So the study of elastomeric PU/clay nanocomposites have been studied extensively^[7-9]. Pinnavaia and his coworker^[10] first report their work in this field. They mainly focused on compatibility between organo-clay and polyols, and their work showed that a good compatibility was founded between smectite (montmorillonite) clay exchanged with long chain onium ion(carbon number ≥ 12) and several polyols commonly used for preparation of polyurethane. Chen^[7] developed a two-stage synthesis of polyurethane/clay nanocomposites by synthesizing polycaprolactone(PCL)/clay nanocomposite and then by replacing a part of 1, 4-Butanediol (1, 4-BD) with the synthesized PCL/clay nanocomposites to form PU/clay nanocomposites. For Chen's another work^[8], amount of organoclay mixed with DMF solvent directly disperse in PU to probe their effect on the thermal, mechanical and water absorption properties of PU. Qi^[9] also report the synthesis and characterization of elas-

tomeric polyurethane/clay nanocomposites, and gave the effect of organo-clay percentage on the mechanical and thermal properties of the PU polymers.

All the previous works employed organoclay by directly dispersed in pure PU, and no significant improvement about the properties were observed. Compared to the former, we employ inorganic clays such as kaonilite and smectite clays, and directly react with NCO group terminated polyurethane polyelectrolyte to get real novel segmented PU/clay nanopolymer to improve the properties of pure polyurethane.

In this paper, the probability of reaction for the clays with isocyanate group will be discussed. The morphology, internal structure and chemical composition for the clays will be characterized by TEM-EDX, and the presence of hydroxyl group and the effect of temperature on the stability of the OH group will also be investigated in detail.

The objectives of this paper are to understand the microstructure, chemical composition and the morphology of kaolinite clay, and further to probe the possible reaction probability of kaolinite clay with isocyanate(NCO) group terminated PU polyelectrolyte prepolymer.

1 Experiment and Material

Commercial clay, kaolinite coming from commercial company was characterized by Transmission electron microscopy(TEM), TGA and PAS FTIR respectively. Morphology for kaolinite was examined by TEM, a Philips CM20 200kV electron microscope equipped with a charge-coupled device (CCD). The CCD camera produce electronically enhanced image contrast, allowing extremely thin objects to be viewed at high resolution. Use of the TEM in the diffraction mode produced standard electron diffraction pattern that gave the information of their clay morphology.

PAS-FTIR spectra were recorded with a Bruker spectrometer, Model IFS66. All spectra were recorded by using the same MTEC 100 photoacoustic cell, and by the following procedures:

- (1) Open the Valve of Helium, assure enough

pressure of helium to remove CO_2 and moisture 20 ~ 30min.

(2) Start the FTIR software, set the same parameters for background and sample collection, and click the COLLECT button, the spectra was then collected.

Thermal Gravimetric Analysis (TGA) curve was recorded by Instruments TGA 2950, under the operation conditions of temperature rising from 20°C to 800°C at the rate of $20^\circ\text{C} \cdot \text{min}^{-1}$, and the N_2 as carrying gas.

2 Results and Discussion

2.1 Transmission Electron Microscopy (TEM)

TEM image for kaolinite clay in Fig. 1, the size of selected kaolinite plate is over 1000nm. Around the large plate, there are many small size plate particles. Most of them showed the small hexagon shape. TEM image also showed that the large hexagon shape is a stacked pack of small plates in the lower right for kaolinite. The size of some particle varied from the smaller to the larger due to the presence of electrostatic cohesive energy and a certain degree of hydrogen bonding between one layer and the adjoining layer, they often stacked together to form a thick plate particle. The results of EDX gave the composition ratio of

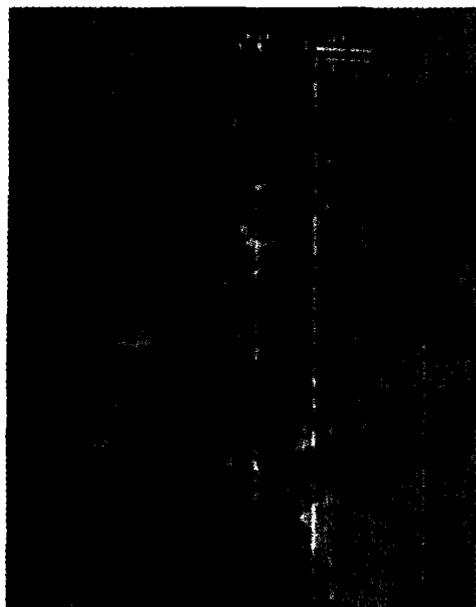


Fig. 1 TEM image for kaolinite clay

1.8 for Si/Al. It means that there is much Al atom in kaolinite clay. And therefore, the adsorption of structural hydroxyl group attached on Al atom was strong. It was clearly observed in PAS FTIR spectra in Fig. 3. More detailed discussion was seen Characterization of PAS FTIR for kaolinite clay. Image of selected X-ray diffraction showed that the microstructure of single thin kaolinite plate perform typical single crystalline, seen in Fig. 2.

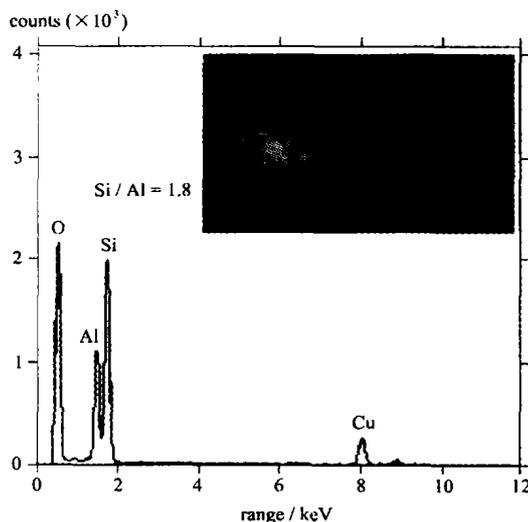


Fig. 2 TEM image and EDX result for kaolinite clay

2.2 PAS-FTIR spectrometer (bulk analysis)

PAS-FTIR spectra at room temperature for kaolinite clay are shown in Fig. 3. This technique directly probes chemical bonds and is particularly suitable for the characterization of powder samples with strong IR absorption characteristics, providing compositional and structural information. Because layers several μm thickness were probed, the application of PAS-FTIR to ultra-fine solids was considered to be a bulk technique. For kaolinite, the presence of Al or Si is indicated by intense peaks positioned at about 470cm^{-1} , 550cm^{-1} in finger region^[11]. A medium peak at 915cm^{-1} for kaolinite attributed to the OH bending mode from Al-OH, the peaks at 1028cm^{-1} and 1105cm^{-1} originating from Si-O the stretching vibration.

Between $4000 \sim 3000\text{cm}^{-1}$ in hydroxyl region, it is clearly observed that both samples showed little significant difference. The band at 3744cm^{-1} corre-

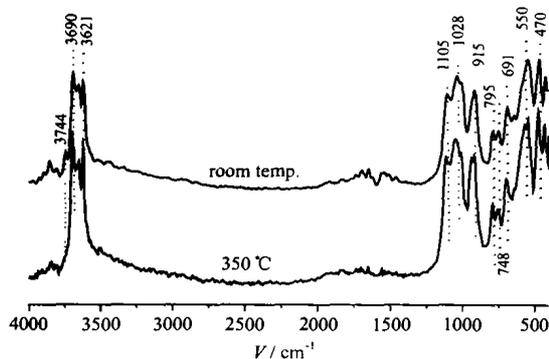


Fig. 3 PAS FTIR Spectra for kaolinite clay at room temperature and treated at 350°C for 3h

sponding the free OH stretching mode of Si-OH, and the peaks at 3690cm^{-1} and 3621cm^{-1} contributed by stretching of hydrogen bonded structural OH on the surface of the clays. Farid^[11] attributed the band at 3690cm^{-1} to the stretch of Al-OH. At room temperature, both the absorption of hydration water between $3500 \sim 3000\text{cm}^{-1}$ and a isolated medium band assigned to its bending mode at 1650cm^{-1} could not be detected for the two samples, seen Fig. 3. After treated at 350°C for 3h, the spectra almost kept the same.

2.3 Thermal Gravimetric Analysis (TGA)

Besides of analysis of TEM, EDX and PAS-FTIR, thermal gravimetric analysis (TGA) is another useful tool for the characterization of clay minerals. Fig. 4 gave the weight loss of clays by means of thermal balances of varied design.

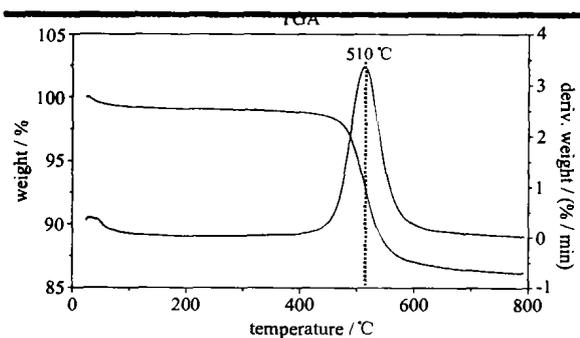


Fig. 4 TGA curve for kaolinite clay

In Fig. 4, Only one weight loss peak occurred around 510°C. This peak indicated the loss of structural hydroxyl groups in the form of water (dehydroxylation), then the weight of kaolinite kept stable again.

However, the weight loss peak around 60°C was not clear, it indicated that there is little hydration water absorbed on the surface of kaolinite particle, and little weight loss at this temperature. The result was consistent with the result of PAS-FTIR analysis.

From our results, it could be concluded that the structural hydroxyl groups on the surface of clays was very stable below 500°C, and it could act as other organic compound containing hydroxyl groups to react with NCO terminated polyurethane prepolymer to manufacture novel segmented nanoclay composited polymer. It should be pointed out that these clays should be first treated by removing little moisture adsorbed by clays, otherwise, it will lead to the failure to manufacture the nano clay composited polyurethane polymers. We will report preparation of nano composites soon.

3 Conclusion

Nano kaolinite clay used in polymer composite has been characterized by TEM, TEM-EDX, PAS-FTIR and TGA. The TEM/EDX data showed that the kaolinite has a larger particle size and a Si/Al ratio of 1.8. The individual particle of kaolinite platelet was a single crystalline. TEM also showed that kaolinite particles were stacked by platelets. The TGA results revealed that kaolinite almost doesn't lose weight around 60°C. However, kaolinite lose weight much around 510°C and lose its structural hydroxyl functional group. The PAS-FTIR spectra showed that kaolinite had little absorbance of hydroxyl group for hydration water in hydrogen bond region at room temperature, suggesting a very weak ability to adsorb water on kaolinite particle surface. The result was very consistent with that of TGA analysis. Therefore, it could be concluded that the structural hydroxy groups on the surface of clays was very stable below 500°C, and it could act as other organic compound containing hydroxyl groups to react with isocyanate group terminated polyurethane prepolymer to manufacture novel segmented clays composited polymer.

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