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Surface modification of calcined kaolin with toluene diisocyanate based on high energy ball milling

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ABSTRACT

The surface of calcined kaolin particle was modified with toluene diisocyanate (TDI) by using high energy ball milling. The prepared hybrids were characterized by FT-IR, MAS NMR, thermal analysis (TGA-DSC), static water contact angle (CA), apparent viscosity and transmission electron microscopy (TEM). FT-IR and MAS NMR spectra demonstrated that TDI molecules were chemically anchored to kaolin surface after modification. The results of thermal analysis showed that the maximum grafting ratio reached up to 446.61% when the mass ratio of TDI/kaolin was 0.5:1.0, and CA measurements revealed that the resultant hybrids exhibited strong hydrophobicity (148.82°). Apparent viscosity and TEM were employed to examine the dispersion properties of blank and modified kaolin particles in poly (dimenthylsiloxane) matrix. The results illustrated that the dispersion stability depended strongly on the grafting ratio of TDI, neither too low nor too high achieved uniform and stable dispersion, and the favorable grafting ratio was obtained when the mass ratio of TDI/kaolin was 0.2:1.0. Further modification of TDI/kaolin (mass ration of TDI/kaolin, 1.0:1.0) particles with bis(aminopropyl)-terminated-poly(dimethylsiloxane) (APS) was also investigated. TEM evidenced that the dispersion properties of the obtained TDI/APS/kaolin particles were remarkably improved in octamethyl cyclotetrasiloxane compared with the original TDI/kaolin particles.

1. Introduction

Because of its excellent performances such as high whiteness, good bonding ability and great electrical insulating property, kaolin or kaolinite has already become an indispensable material for many industrial processes, including paper manufacture, paints, ceramics, rubber, plastics and other engineering applications [1–6]. Over the past few decades, kaolin/polymer composites have occupied a prominent position in material science, because they often exhibit remarkable improvement in mechanical properties, thermal stability and flame retardancy even at rather low loading [7–9]. Actually, natural kaolin is not compatible with hydrophobic polymer matrix, which has been generally attributed to the lack of affinity between them. Thus, it is essential to modify kaolin in an applicable way to improve the interaction between guest kaolin particles and host polymer matrix prior to the preparation of kaolin/polymer composites.

Ion exchange using quaternary ammonium salt is a common approach for kaolin surface modification. González et al. reported that natural kaolin could be modified using diallyldimethylammonium chloride in aqueous medium under alkaline condition, and the obtained kaolin particles were found to be appropriate elastomer filler [10]. However, the modification effect of this method strongly depends on the cationic exchange capacity (CEC) of kaolin, rather than on which kind of quaternary ammonium salt used in the ion exchange process. Unfortunately, crude kaolin has low CEC about 0.03–0.25 mol/kg due to the low level of isomorphous substitution within the lattice structure [11]. What is worse, some objections have also been raised that the modified particles prepared in this way would be thermodynamically immiscible with polymer matrix at a high temperature [12,13]. Taking into consideration these aspects, ion exchange is not practicable for kaolin modification in most cases even though quaternary ammonium salt is cheaper than some other modifiers such as silane coupling agents.

Grafting modification is generally considered to be an attractive and effective method to render clay particles (e.g. kaolin and montmorillonite) more compatible with polymeric matrix. For familiar kaolin (namely layered kaolin), however, one problem should be primarily settled prior to the grafting procedure, which means the strong van der Waals force and hydrogen bonds between consecutive layers of kaolin. Both of them make more difficult the access to Al-OH groups of the interlayer space [14,15]. In order to overcome this problem, some small intercalation agents

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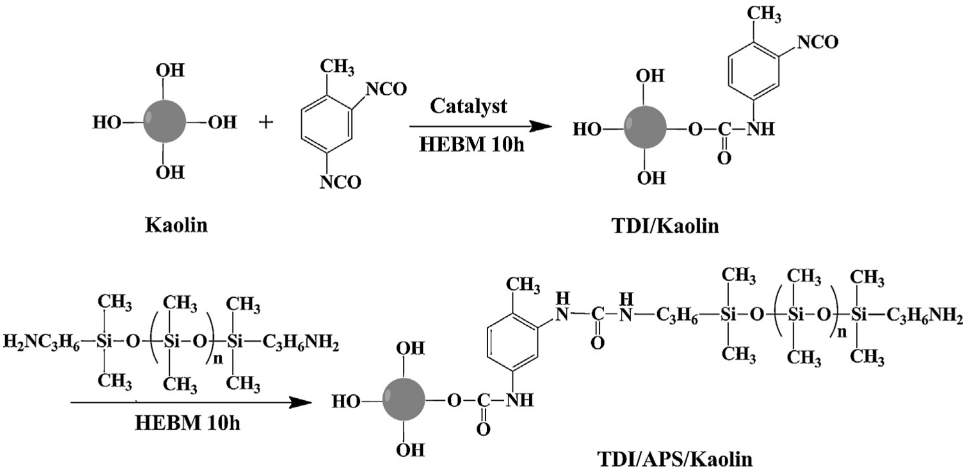

Fig. 1. General schematic of surface modification of calcined kaolin particles with TDI and APS.

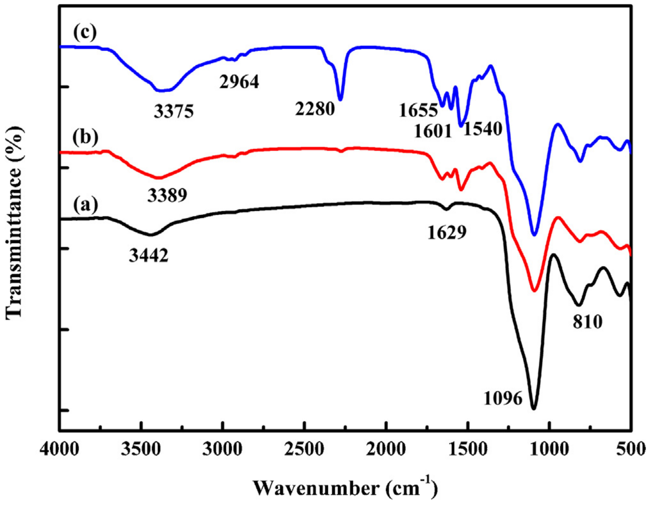

Fig. 2. FT-IR spectra of blank kaolin (a) and TDI/kaolin particles (mass ratio, 0.2:1.0 (b) and 1.0:1.0 (c)).

with high dipole such as cesium acetate and dimethyl sulfoxide [16–19] were employed to enlarge the space between two adjacent layers of kaolin, followed by the interlayer grafting onto aluminol groups of kaolin with functional organic molecules that possess versatile properties, especially hydrophobicity. Therefore, it is convincingly concluded that the grafting modification process of layered kaolin particles involves at least two steps: the primary introduction of intercalation agents and the subsequent modification with grafting compounds. From another point of view, however, if calcined kaolin particles are employed as starting material rather than layered kaolin, the grafting modification shall be performed directly skipping the intercalation step. Moreover, previous study stated that a considerable number of reactive sites shall be preserved on the calcined kaolin particle surfaces although most of hydroxyl groups are removed during the calcination process [20]. Consequently, the grafting modification of calcined kaolin with particular modifier with highly active groups is convenient under specific conditions compared with layered kaolin and feasible in theory.

Toluene diisocyanate (TDI), which is very active to hydroxyl group even under a gentle condition due to the unsaturated isocyanate groups, was usually utilized to modify nano-sized silica particles to enhance its hydrophobicity, and the introduced isocyanate group was served as bridging unit to acquire further modification [21,22]. To the best of our knowledge, reports on the chemical modification of calcined kaolin particle surface are quite scarce, let alone using TDI as activating agent. Thus, TDI was applied to modify calcined kaolin in the present study.

High energy ball milling (HEBM) was often used as simple mixing device in industrial applications, and in particular it was also considered as an available approach to break-up and split aggregates and agglomerates of particles in laboratory. Recently, Dabhade et al. reported that nano-sized titania powders (average particle size of 35 nm) was successfully synthesized from titanium particles of 2 μm primary particle size by high energy milling at suitable milling parameters [23]. González-Benito et al. fabricated

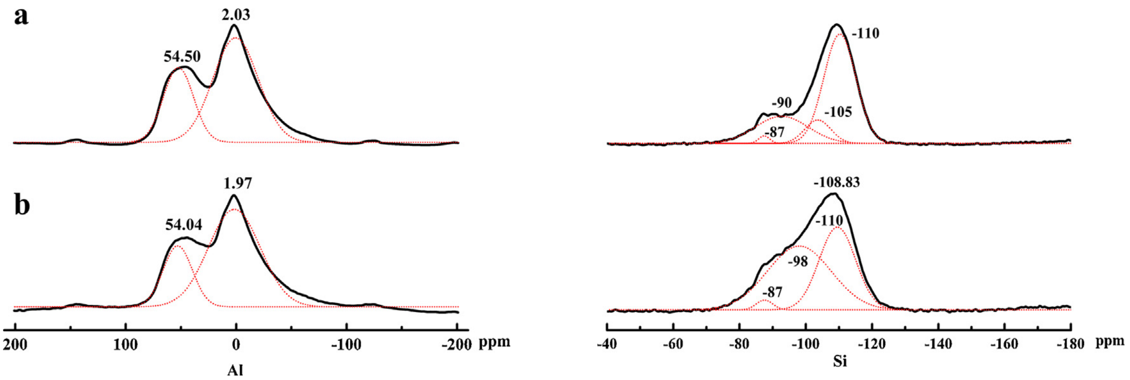

Fig. 3. ^{29}Si and ^{27}Al MAS NMR spectra of blank kaolin (a) and TDI/kaolin particles (b) (solid lines: experimental spectra, dotted lines: simulated spectra).