



Research paper

Influence of interlayer functionalization of kaolinite on property profile of copolymer nanocomposites

Sonia Zulfiqar^{a,b,*}, Muhammad Ilyas Sarwar^{a,c,**}, Nagina Rasheed^c, Cafer T. Yavuz^d^a Department of Chemistry, School of Natural Sciences (SNS), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan^b Institute for Polymer Materials, POLYMAT, University of the Basque Country (UPV-EHU), Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia–San Sebastian, Spain^c Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan^d Graduate School of EEWS, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

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ABSTRACT

Nanocomposites of co-poly (vinyl chloride–polyvinyl acetate–polyvinyl alcohol) (PVC–PVAc–PVA) and kaolinite were prepared via solution intercalation technique. To improve compatibility among the phases and to expand the interlayer basal spacing, kaolinite was modified using dimethylsulfoxide (DMSO) as a swelling agent. The influence of kaolinite dispersion and interaction between the disparate phases on the properties of nanocomposites were investigated using Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), mechanical testing, thermogravimetric analysis (TGA) and water absorption measurements. IR data confirmed the hydrogen bonds formed between DMSO and the surface hydroxyl groups of kaolinite. XRD and microscopic results revealed that clay mineral was intercalated with uniform dispersion at nanoscale in the matrix. Tensile testing of these materials indicated significant improvements in the mechanical properties relative to the pure copolymer. Incorporation of kaolinite into the organic phase enhanced the thermal stability of the nanocomposites. Water absorption of the nanomaterials was reduced upon the addition of modified kaolinite rendering decreased permeability with increasing dispersibility of clay mineral in the copolymer matrix.

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1. Introduction

Nanocomposites are a unique and important class of nanomaterials produced from the ultimate blending of organic and inorganic phases at nanoscale (Alvi et al., 2014). Among the inorganic phases, clay minerals exhibit a pivotal role and the most widely exploited minerals are phyllosilicates, especially the smectites (Zahra et al., 2014). Intercalation is the prerequisite for complete delamination of silicate layers in the organic matrix, leading to the formation of nanocomposite materials (Alvi et al., 2013). Due to the ample swelling behavior, montmorillonite (Mt) is the most employed clay mineral for the fabrication of nanocomposites with potential high-tech applications (Theng, 1979; Alexandre and Dubois, 2000; Pinnavaia and Beall, 2000; Viville et al., 2003). It is believed that kaolinite is originally produced by chemical weathering of igneous rocks containing the feldspar and is an abundantly available clay mineral having chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Ruiz-Hitzky

and Meerbeek, 2006). Kaolinite is a 1:1 layered dioctahedral aluminosilicate formed by silicon tetrahedral sheets and aluminum octahedral sheets. The individual layers are connected together by van der Waals and hydrogen bonds that limit the access to aluminol groups for grafting reaction. They are linked also by the strong dipole interactions between the asymmetric layers. As a result, kaolinite has been described as non-expandable for a long time, until it was revealed that some polar molecules could be intercalated into the interlayers of kaolinite. This clay mineral is an inexpensive additive that can improve the properties of materials (Bailey, 1988; Pinnavaia and Beall, 2000; Alkan et al., 2005; Turhan et al., 2010) and is widely used in industry as paper or cosmetics additive, and in ceramics. However, interlayers of kaolinite are not easily accessible; its interlayer chemistry is much less developed than Mt. Therefore, only few reports on kaolinite intercalation and nanocomposite formation are encountered in literature relative to Mt (Tomposon and Cuff, 1985; Ledoux and White, 1996; Cabeda et al., 2004; Alkan et al., 2008; Elbokl and Detellier, 2008; Li et al., 2008; Karaoglu et al., 2009; Mbey et al., 2012). Various swelling agents have been employed for kaolinite intercalation including DMSO, N-methylformamide (NMF), potassium acetate, hydrazine, urea, cyclic imides and methanol (Tomposon and Cuff, 1985; Uwins et al., 1993; Ledoux and White, 1996; Komori et al., 1998; Frost et al., 1999; Elbokl and Detellier, 2008).

Nanohybrid materials have been prepared from the grafting of 3-aminopropyltriethoxysilane onto the internal aluminol groups of

* Correspondence to: S. Zulfiqar, Department of Chemistry, School of Natural Sciences (SNS), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan. Tel.: +92 51 90855608; fax: +92 51 90855552.

** Correspondence to: M.I. Sarwar, Department of Chemistry, School of Natural Sciences (SNS), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan. Tel.: +92 51 90855578; fax: +92 51 90855552.

E-mail addresses: soniazulfiqar@yahoo.com (S. Zulfiqar), ilyassarwar@hotmail.com (M.I. Sarwar).

kaolinite previously intercalated with DMSO or urea. The modified kaolinite was coated on a platinum electrode as electrochemical sensors to leach out $[\text{Ru}(\text{CN})_6]^{4-}$ anions through multi-sweep cyclic voltammetry. Similarly, a range of compounds bearing hydroxyl groups were successfully grafted onto the OH groups of kaolinite yielding amino-functionalized kaolinite derivative. These derivatives were robust nanohybrid materials, decomposing at temperatures above 300 °C and resisting hydrolysis (Tonle et al., 2007). A series of organic–inorganic nanohybrid materials have been achieved by the intercalation of ionic liquids based on imidazolium derivatives in the interlayer spaces of kaolinite. Intercalation with imidazolium salts augmented the thermal stability of the resulting materials by more than 150 °C with respect to DMSO–kaolinite intercalate. The observed high thermal stability is promising for the use of these nanohybrid materials as precursor for the synthesis of new nanocomposites by incorporation of polymer in kaolinite at high temperature (Letaief and Detellier, 2007). In another related attempt, electrical conductivity of kaolinite nanohybrid materials prepared from the intercalation of ionic liquids based on imidazolium derivatives was measured at various temperatures. The imidazolium cations aligned to form alternating tunnels of organic cations and halide anions resulted in the highest ionic conductivity in a temperature range of 160–200 °C. At higher temperatures, the conductivity dropped dramatically due to the decomposition of organic material and the resulting collapse of the structure. The conductivity trend was highly dependent on the structure of the imidazolium derivatives (Letaief et al., 2008). Kaolinite–PVC nanocomposites were fabricated by dispersing the nanolayers into PVC matrix by the solution intercalation method (Turhan et al., 2010). The organophilicity of kaolinite was improved when intercalated with DMSO. Thermal stability of the nanocomposites was improved and transparency was increased relative to pure PVC but reduced with increase in kaolinite in the nanocomposites.

Herein we report the synthesis and characterization of PVC–PVAc–PVA and modified kaolinite nanocomposites using solution intercalation technique. Intercalation of kaolinite was carried out with DMSO for ample compatibility between the organic and inorganic phases. Modified kaolinite is suitable as filler in the preparation of polymeric nanocomposites. Tetrahydrofuran (THF) was used as reaction solvent for the preparation of nanocomposites. Different compositions of the nanocomposites containing 1 to 20–wt.% modified kaolinite were prepared. Thin composite films obtained after evaporating the solvent were subjected to FTIR, XRD, TEM, SEM, TGA, tensile testing and water absorption measurements.

2. Experimental

2.1. Chemicals

Co-poly(vinylchloride–vinylacetate–vinylalcohol) with an average $M_n = 27,000$, having a composition of vinylchloride, vinylacetate, and vinylalcohol, 90, 4, and 6 wt.% respectively and kaolin with chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ were obtained from Aldrich. The copolymer was used after drying under vacuum at 50–52 °C for 24 h. DMSO was procured from Riedel–de Haen and used as received. Tetrahydrofuran (THF) purchased from Merck was first distilled at constant boiling temperature, followed by the addition of anhydrous calcium oxide left overnight. After distillation, it was refluxed over sodium wire with benzophenone as an indicator. The deep blue color of the solution confirmed the drying of THF, which was then collected and used as solvent.

2.2. Intercalation of kaolinite with DMSO

Modification of kaolinite was carried out with DMSO as a swelling agent. For this purpose, kaolinite (3 g) was charged into the round bottom flask and then mixed with DMSO (60 ml). The reaction mixture was agitated at 80 °C for 120 h. The modified clay mineral was filtered and washed with methanol to ensure the complete removal of excess

DMSO. Modified kaolinite was dried in vacuum oven at 100 °C for 24 h. The dried cake was ground and screened with a 50 μm sieve. The modified kaolinite was labeled as K-DMSO and employed in the preparation of nanocomposites.

2.3. Preparation of nanocomposites

Nanocomposites were prepared by mixing appropriate amounts of K-DMSO and copolymer solution. For this purpose, a stock solution of the copolymer was prepared in dried THF (100 g) by dissolving 12 g of copolymer. For a particular concentration of nanocomposite fabrication, a known amount of the copolymer solution was taken in 50 ml flask and then stoichiometric amount of modified kaolinite was added. The resulting solution was agitated for 24 h at 25 °C. Similar procedure was followed for the preparation of other compositions of hybrids with different clay content. Thin films were cast in clean glass petri dishes by placing them on a leveled surface. Solvent evaporation was carried out at 40 °C for 24 h. These hybrid films obtained were then further dried in vacuum for 20 h in order to remove the solvent completely up to a constant weight.

2.4. Characterization

UV–vis transmission spectra of the pure copolymer and composite films were recorded using Shimadzu Spectrophotometer. The structural elucidation of copolymer matrix, kaolinite, K-DMSO and thin nanocomposite films was carried out by using Excalibur series Thermo Nicolet 6700 FTIR spectrophotometer, over the range of 4000–500 cm^{-1} in the ATR mode. The diffraction behavior of neat kaolinite, K-DMSO and nanocomposites was studied using X-ray diffractometer Model XPert Pro 3040/60 PANALYTICAL with Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 30 mA). The scanning angle for all measurements was kept between $2\theta = 5^\circ$ and 50° . The morphology of copolymer/kaolinite nanocomposites was investigated by recording the images using FEI Tecnai G2 Spirit Twin transmission electron microscope, operated at an accelerating voltage of 120 kV. The nanocomposite films were first microtomed into 30 nm ultra thin sections with the help of diamond knife using Leica Ultracut UCT ultramicrotome. SEM images of powdered kaolinite sample and cryo-fractured composite films were recorded with the help of scanning electron microscope Model JEOL JSM-6490LA operated at 20 kV. Tensile properties of the nanocomposite films were measured according to DIN procedure 53455 using Testometric Universal Testing Machine M500-30, and an average value obtained from five to seven different measurements in each case has been reported. Thermal stability of the nanocomposites was determined using NETZSCH TG 209F3 thermogravimetric analyzer by using 1–5 mg of the sample in Al_2O_3 crucible heated from 25 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere with a gas flow rate of 20 ml/min. The water uptake of these materials was carried out under the specifications of ASTM D570-81. Pure copolymer and nanocomposite films were first oven dried, cut to equal dimensions and then weighed to get the initial weight (W_o). The films were immersed in deionized water at 25 °C. After every 24 h, the films were taken out from water and were placed between the sheets of the filter paper to remove excess water and then weighed instantly. The films were again dipped in water and the process of weighing was repeated after every 24 h until the films reached constant weight (W_f). The total soaking time was 96 h because it was found to be enough for attaining equilibrium. The percent increase in weight of the films was calculated by using the formula $(W_f - W_o) / W_o$.

3. Results and discussion

The pure copolymer film obtained was transparent and the hybrid films were transparent to opaque with whitish color. The films became semitransparent and opaque as well as brittle with higher K-DMSO content. The mechanical behavior of hybrid films was recorded at ambient

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