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Preparation and Characterization of the Inorganic－Polyvinyl Alcohol Layered Nanocomposites

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Abstract

This work focused on the preparation of poly (vinyl alcohol) (PVA)/inorganic composites. Montmorillonite (MMT) and organically modified montmorillonite (OMMT) were used as the inorganic compounds. PVA/MMT and PVA/OMMT nanocomposites were prepared by solvent solution method. The morphology and interlayer spacing of the composites were characterized. Furthermore, the reaction mechanism between these Montmorillonites (MMT) and PVA was suggested that the hydrogen bonding and hydrophobic interactions contribute to the preparation.

Keyword: Poly (vinyl alcohol), montmorillonite, organically modified montmorillonite, ionic interaction, hydrogen bonding.

1. Introduction

In recent years, much of attentions have been concentrated to study nanocomposites build from inorganic layered materials and various polymers. Inorganic-polymer nanocomposite often exhibited remarkable improvement of various properties such as mechanical property, thermal stability, and photochemical stability [1] [2].

Poly (vinyl alcohol) (PVA) is a synthetic polymer of great industrial importance. PVA has been applied wide range of fields because of particular properties such as water soluble and adhesive properties. Moreover PVA is known as ecological polymer due to its biodegradability. Fernandes et al. [3] exhibited PVA/modified lignin (KLD) blends. KLD was found to grow antioxidant/photo-protective properties to PVA. In PVA/KLD films, an improvement of thermal stability was confirmed, compared to the film of pure PVA, due to KLD incorporation and also due to irradiation, through thermogravimetry. Sionkowska et al. [4] exhibited PVA/collagen blends. The product possessed different thermal and photochemical stabilities than those of single components.

Nanocomposites based on PVA and organic compound have been studied. In this work, inorganic layered materials were used especially for the preparation of inorganic-organic layered composites. If inorganic layered material having high thermal and mechanical stabilities was filled in polymer matrix, the property of the products increased due to intermolecular interactions, in which polymer chains were intercalated into inorganic interlayer.

In the field of polymer blend investigation, MMT has been studied widely because polymer/MMT blend improved various properties when compared with the pure polymer [5] [6]. MMT easily interposed organic compounds in the interlayer space. MMT modified with *n*-hexadecyl-ammonium cation organically modified montmorillonite (OMMT) was used as an organically modified layered silicate for the nanocomposites preparation. The increase of interlayer range was analyzed by X-ray diffraction. OMMT also interposed basically monomers and polymer in the gallery space.

This work focused on the preparation of PVA/MMT and PVA/OMMT nanocomposites. The morphology and interlayer spacing of composites was characterized by X-ray diffraction (XRD) patterns, thermogravimetric analysis (TG), and scanning electron microscopy (SEM). Furthermore, the reaction mechanism between PVA and MMT or OMMT was studied

2. Experimental

2.1 Materials

Poly (vinyl alcohol) (Mw=89,000- 98,000) with a degree of hydrolysis of 99+% was purchased from Sigma-Aldrich. The Na^+-type montmorillonite (MMT-Na) was provided by the Kunimine Co. Ltd. The cation-ion exchange capacity (CEC) of MMT-Na was found to be 119 meq/100g. The *n*-hexadecyamine was obtained from Tokyo Kasei Company and the Cica-reagent grade hydrochloric acid was purchased from Kanto Chemical Co., INC.

2.2 Methods

2.2.1 *Preparation of the organomodified montmorillonite (OMMT)*

n-Hexadecylamine 0.145mol and 2ml HCl were dissolved in 200ml distilled water under constant stirring. Then MMT 10g were dissolved into 500ml distilled water stirring at 353K for 1h. The organo-modified montmorillonite composites were obtained from filtering the mixture after stirring at 353K for 1h.

2.2.2 *Preparation of Inorganic-Organic Layered Nanocomposites*

PVA 0.3g and OMM (or MMT) 0.7g was dissolved in 40ml distilled water under constant stirring for 1h at 353K. Then the mixture was filtered and dried at room temperature.

3 Results and Discussions

3.1 Characterizations of OMMT

The SEM images of unmodified montmorillonite (MMT) and OMMT are shown in Fig.1. OMMT, MMT modified by *n*-hexadecylamine shows a smooth surface as shown in Fig.1

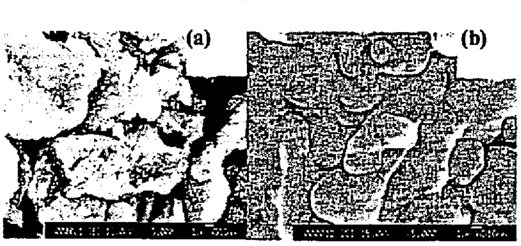

Fig.1. SEM images of (a) MMT and (b) OMMT

IR spectra of the MMT and OMMT showed four bands at around 2917cm^{-1}, 2846cm^{-1}, 1417cm^{-1}, and 727cm^{-1} indicating the presence of methylene (-CH_2-) and methyl (CH_3) groups, and also showed two bands at 3251cm^{-1}, 1612cm^{-1}, and 1700cm^{-1} indicated the presence of amine (CH_2-NH_3^+) as shown in Fig.2.

XRD patterns of the products were shown in Fig.3. The interlayer spacing of OMMT increased from 1.21nm of the MMT to 1.74nm. It suggested intercalation of *n*-hexadecylamine in the interlayer space of MMT.

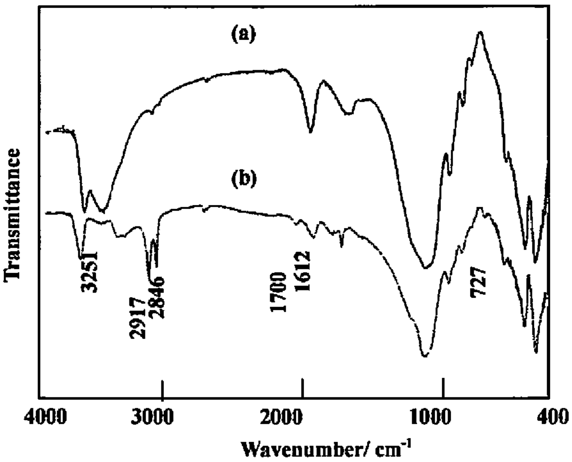

Fig.2 FT-IR spectra of (a) the MMT and (b) OMMT

The chemical analysis of the OMMT indicated that the nitrogen content was 1.10wt%. The same results were obtained from TG profiles. The amount of *n*-hexadecylamine between the layers was estimated as 24%.

3.2 Characterization of PVA/MMT and PVA/OMMT

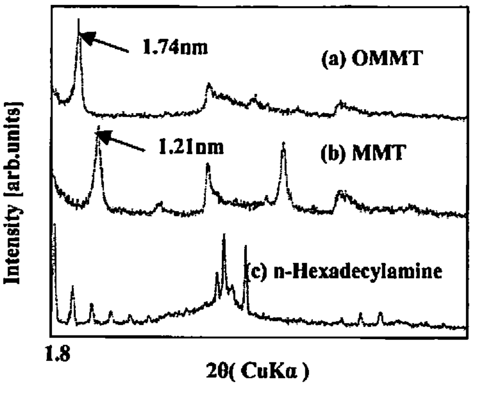

Fig.3 XRD patterns of (a) OMMT, (b) MMT, and (c) *n*-hexadecylamine.

XRD patterns for PVA, MMT, OMMT, PVA/MMT and PVA/OMMT are shown in Fig. 4. The diffraction pattern for the MMT (Fig.4b) shows a typical layered structure with a basal d-value of 1.21nm. After the reaction with the PVA the interlayer spacing increased to1.77nm (Fig.4d).

And the similar change was observed in the cases of OMMT to PVA/OMMT. The d-value increased from 1.74nm (Fig.4c) of OMMT to 2.41nm (Fig.4e) of the PVA/OMMT as shown in Fig.4.

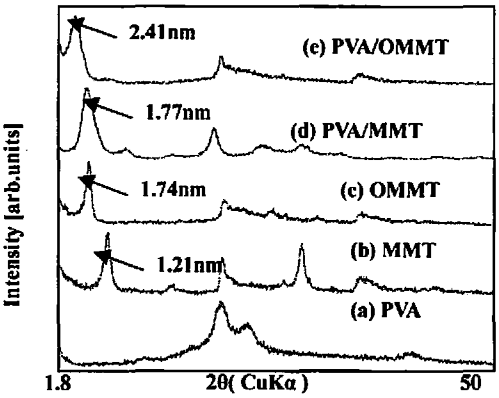

Fig.4 XRD patterns of (a) PVA, (b) MMT, (c) OMMT, (d) PVA/MMT and (e) PVA/OMMT

The SEM images of the PVA, PVA/MMT and PVA/OMMT were shown in Fig5. Morphology of PVA was a mass of some fine particles (Fig.5c). Then the morphology of PVA/MMT and PVA/OMMT were different with those of PVA, MMT or OMMT completely.

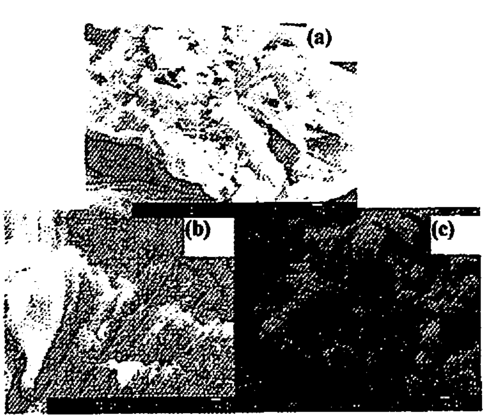

Fig.5. SEM image of (a) PVA/OMMT, (b) PVA/MMT and (c) PVA

The above results indicated that the intercalation into the interlayer space of MMT or OMMT occured by the interaction between the PVA and MMT or OMMT. Generally the chain length of the PVA was long and crossing, it is very difficult to contain the entire of the PVA polymer chain between the layers. However, the TEM image of the PVA/OMMT (Fig.6), clearly indicated the presence of layer structures. So the part of PVA chains or some small molecular chains were intercalated into the inorganic layers by the interaction, resulted the increment of the interlayer space.

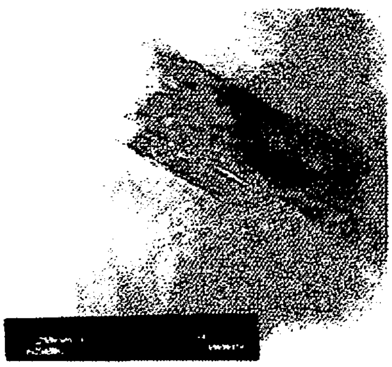

Fig. 6 TEM image of PVA/OMMT

In the stage of the enterprise which reacted from MMT to OMMT, ionic interaction was expected between the positive charge of hexadecylamine and negative charge of the plane of MMT. The ionic interaction caused the increment of the interlayer space.

And in the next stage of the reaction of OMMT with PVA, two kinds of interactions are expected. The first one was the hydrogen bonding. The MMT consists of 2 tetrahedral sheets (SiO_2 tetrahedron) sandwiching a central octahedral sheet (Al_2O_3, MgO, FeO). That is, the surface of the layer plate is the SiO_2 tetrahedron, the combination between the surface of the layer plate and the hydrogen bonding in PVA was magnified. Hydrogen bonding was formed between Si-O bonding and O-H bonding. And the second one is that hexadecylamine remained in the interlayer of the OMMT, and the aminobonding hand was glued to the surface of the layer flat, and the other hand the aliphatic hydrocarbon of the hexadecylamine was placed into the interlayer of MMT, which play as the hydrophobic spaces. That is to say, the surface of the layers was indicated the hydrophilicity, and

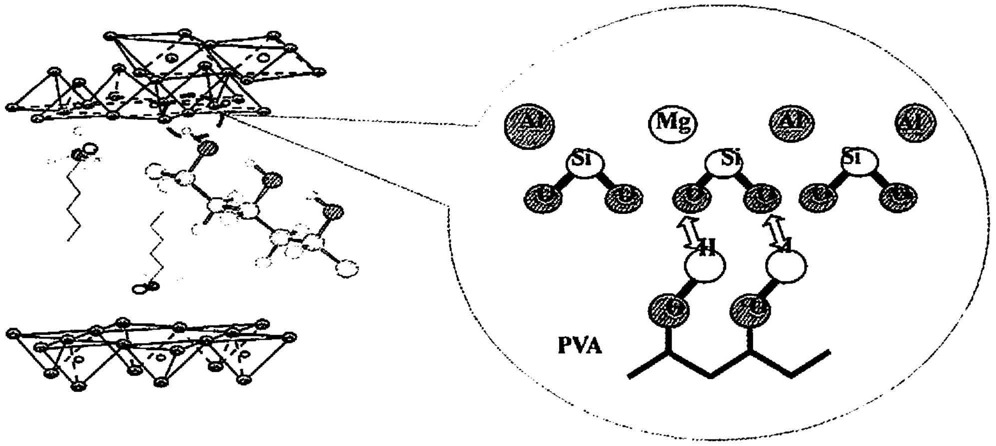

Fig.7 The mechanism of reaction between PVA with OMMT.

the inside of layers was shown as the hydrophobicity, in which the aliphatic hydrocarbon of PVA was easy to insert into the inside of the OMMT layers. The process resultes from the intercalation reaction between OMMT and PVA. In the case of the MMT, the reaction was caused by hydrogen bonding. Therefore the interlayer space 0.56nm increased from 1.21nm of the MMT to 1.77nm of the PVA/MMT, which was smaller than that observed for OMMT in which 0.67nm increased from 1.74nm of OMMT to 2.41nm of PVA/OMMT.

Conclusions

In this study, the preparation of PVA/MMT and PVA/OMMT composites was confirmed for the first time. It was also observed that morphology of PVA/OMMT nanocomposites was lamellar structure similar as OMMT, and the interlayer space of the MMT and OMMT increased after the reaction with PVA. Furthermore, it showed that the hydrogen bond and hydrophobic function caused the interaction between PVA and inorganic compositse.

References

[1]. H. Tian and H. Tagaya, J. Mater. Sci, in press.

[2]. M. Alexandre and P. Dubois, Mater. Sci. Engineer. 28 1/2 (2000) 1.

[3] D.M. Fernandes, Polymer Degradation and Stability, 91, 1192, (2006).

[4] A. Sionkowska, Polymer Degradation and Stability, 83, 117, (2004).

[5]. S. S. Ray, P. Maiti, and K. Ueda Macromolecules, 35 (2002) 3104.

[6]. M. Pluta, A. Galeski, and P. Dubois, Appl. Polym. Sci. 86 (2002) 1497

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