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Dynamic mechanical property and photochemical stability of perlite/PVA and OMMT/PVA nanocomposites

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Abstract This work focused on the preparation of poly (vinyl alcohol) (PVA)/inorganic composites. Perlite and organically modified montmorillonite (OMMT) were used as the inorganic compounds. (PVA)/inorganic nanocomposite films were prepared by solvent solution method. The morphology, dynamic mechanical property, and the photochemical stability of these films were studied. The reaction pathway between these OMMT and PVA was suggested that the hydrogen bonding and hydrophobic interactions contributed to the preparation. The obtained new materials have different thermal, mechanical, and photochemical stability from other single components.

Introduction

In recent years, much attention is being paid to study nanocomposites build from inorganic materials and various polymers. Inorganic-polymer nanocomposites 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 in 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 [3] prepared PVA/modified lignin blends. Modified lignin was found to grow antioxidant/photoprotective properties to PVA. In PVA/modified lignin films, an improvement of thermal stability was confirmed through thermogravimetry, compared to the film of pure PVA, due to modified lignin incorporation into PVA. Sionkowska [4] exhibited PVA/collagen blends. The product possessed different thermal and photochemical stabilities than those of single components.

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

Montmorillonite (MMT), organically modified montmorillonite (OMMT), and perlite were used as the inorganic compounds. PVA/inorganic nanocomposites were prepared by solvent solution method. The morphology and interlayer spacing of the composites were characterized. Furthermore, the presence of interaction between MMT and PVA was suggested in which the hydrogen bonding and hydrophobic interactions contribute to the preparation. In this article, the mechanical properties and the photochemical stability of the blends of PVA and inorganic composites are being studied. The composite was stable photochemically and elasticity was more than that of pure PVA.

Experimental

Materials

Poly (vinyl alcohol) (M_w = 89,000–98,000) with a degree of hydrolysis of 99+% was purchased from Sigma-Aldrich.

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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/100 g. The *n*-hexadecylamine was obtained from Tokyo Kasei Company and the Cica-reagent grade hydrochloric acid was purchased from Kanto Chemical Co., INC. Perlite was supplied kindly by a chemical company.

Methods

Preparation of the organomodified montmorillonite (OMMT)

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

Preparation of inorganic–organic layered nanocomposites

The composites were prepared by mixing suitable amounts of inorganic composites and PVA aqueous solutions at 80 °C for 6 h. The final weight ratios of inorganic compounds were 1 wt.% and 5 wt.%. Polymer film was obtained by casting solutions onto glass plates. After solvent evaporation, the samples were dried at 60 °C.

The samples, in the form of the solutions and films of pure PVA, perlite/PVA, and OMMT/PVA film were irradiated in air at room temperature using a lamp, Riko UVL-400P. The film was submitted to treatment with UV irradiation for 2, 6, 12, and 18 h. To check the change of structure before and after UV irradiation, FTIR spectra were measured.

Characterizations

X-ray diffraction (XRD)

The XRD measurements were performed for MMT, OMMT, and the composites using a RAD-RA diffractometer (RIGAKU Co. Ltd.). Ni-filtered CuKα radiation ($\lambda = 0.154$ nm) was utilized at 40 kV and 100 mA. The samples were scanned in the θ–2θ mode using a step-scanning method with a step-width of 0.05° and 4 s intervals in the range from $2\theta = 2°$ to 50°.

Infrared spectroscopy (FTIR)

IR spectra of the synthesized samples were recorded on Horiba FT200 spectrophotometer in transmittance mode from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 10 acquisitions for each run. All samples were prepared in KBr pellet form.

Dynamic mechanical characterization

The stretch measurements and the dynamic mechanical analysis (DMA) according to the change of the temperature were measured for neat PVA, perlite/PVA, and OMMT/PVA film.

Results and discussions

Morphological characterization

The interlayer spacing of the MMT increased from 1.21 nm to 1.74 nm by organic modification, and the surface state of the chemical bond was confirmed by FTIR and SEM as mentioned in the previous study [5]. It suggested intercalation of *n*-hexadecylamine in the interlayer space of MMT. XRD patterns of the PVA/OMMT and the OMMT/PVA film are shown in Fig. 1. After the reaction with PVA the interlayer space increased to 2.29 nm. Generally the chain length of the PVA is long and crossing, it is very difficult to contain the entire of the PVA polymer chain between the layers. The XRD diffraction patterns indicated the presence of layer structures even after the reaction of OMMT with PVA. So a part of PVA chains or some small molecular chains were intercalated into the inorganic layers.

In the preparation of OMMT, ionic interaction was expected between the positive charge of hexadecylamine and negative charge of the layer plane of MMT.

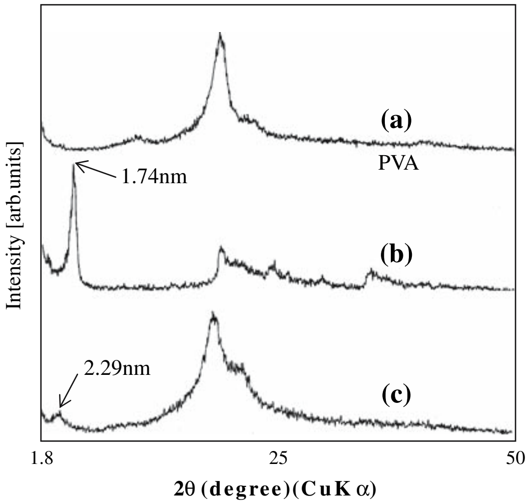


Fig. 1 XRD patterns of (**a**) PVA, (**b**) OMMT, and (**c**) PVA/OMMT

The ionic interaction caused the expansion of the interlayer space.

From the reaction of OMMT with PVA, two kinds of interactions are expected. The first interaction is the hydrogen bonding. The MMT consists of two 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. The second interaction is non-polar interactions. Hexadecylamine remained in the interlayer of the OMMT, and the amino group was glued to the surface of the layer flat, and on the other hand, the aliphatic hydrocarbon of the hexadecylamine was placed into the interlayer of MMT, which form the hydrophobic spaces. That is to say, the surface of the layers was indicated as the hydrophilicity, and the inside of the 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 interlayer space of MMT, 0.67 nm increased to 1.74 nm of OMMT and to 2.29 nm of PVA/OMMT.

Dynamic mechanical characterization

The stretch measurements of the PVA, perlite/PVA, and OMMT/PVA composites were carried out. The results are shown in Fig. 2. From the ratio of stress and strain, the slope of the curve showed the elasticity (G) of the PVA and composites. Perlite/PVA showed the higher elasticity of $G^3 = 2.1$ GPa. Also OMMT/PVA presented more elasticity of $G^2 = 1.57$ GPa than pure PVA of $G^1 = 0.96$ GPa.

The dynamic mechanical analysis (DMA) according to the change of the temperature was measured for neat PVA, perlite/PVA, and OMMT/PVA. The effects of inorganic compound contents on storage modulus (E') and loss modulus (E'') were studied. The results are shown in Fig. 3. The E' and E'' of OMMT/PVA and perlite/PVA composites were higher than that of PVA alone at low temperatures.

The tanδ was obtained by the ratio of E' and E''. The value shows the thermal variation while heating and being pulled. The glass transition temperature (T_g) of the neat PVA, perlite/PVA, and OMMT/PVA composites are shown in Fig. 4. The curves of OMMT/PVA and perlite/PVA showed that the T_g has little shift than the PVA curve. The heat resistance was enhanced by adding the inorganic compounds. The T_g of perlite/PVA composite was suitably higher than that of the OMMT/PVA composite.

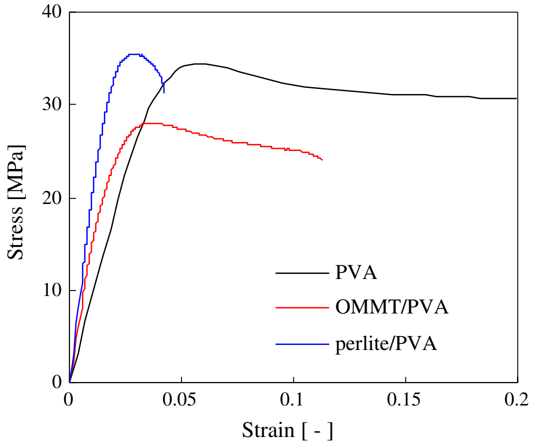


Fig. 2 Stress–strain diagram of PVA film, OMMT/PVA film (5 wt.%), and perlite/PVA film (5 wt.%)

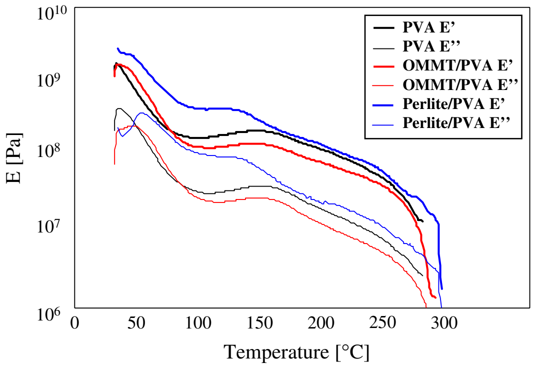


Fig. 3 Storage modulus and loss modulus of PVA film, OMMT/PVA film (5 wt.%), and perlite/PVA film (5 wt.%)

Photochemical stability

The FTIR spectra of OMMT/PVA and perlite/PVA films before and after UV irradiation were compared. Sionkouska presented the photodegradation mechanism of PVA under UV irradiation as shown in Scheme 1 [4]. In this process the C=C stretching and C=O stretching would increase. So to make clear the effect of the inorganic compounds on the characteristics of the composites, FTIR spectra of inorganic composite (1%) and pure PVA were measured from 1,500 cm^{-1} to 1,800 cm^{-1}. The change of the absorbance of C=C and C=O bonds are shown in Figs. 5–7. We can conclude that perlite/PVA and OMMT/PVA films are more stable under UV irradiation than pure PVA. This is confirmed by FTIR spectra. The absorbance of the C=C and C=O bonds after UV irradiation did not increase but decreased.

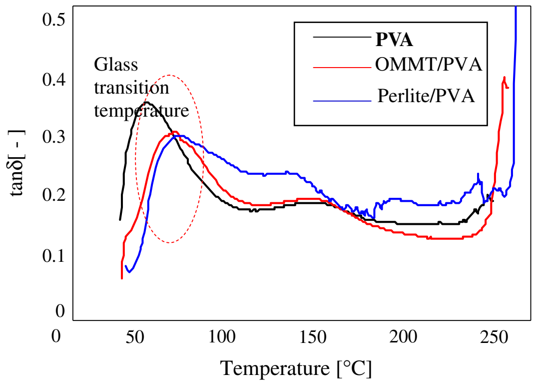
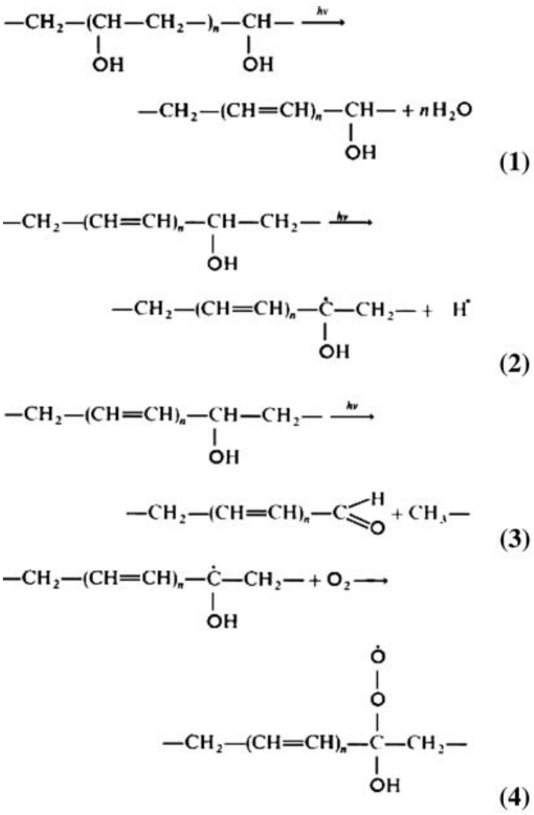


Fig. 4 Loss tangent of PVA film, OMMT/PVA film (5 wt.%), and perlite/PVA film (5 wt.%)

Conclusions

The perlite/PVA and OMMT/PVA films have the possibility as new materials in which some interaction occurs between the inorganic layers and PVA. The interlayer spacing of OMMT increased after the reaction with PVA. Furthermore, it showed that the hydrogen bond and hydrophobic function caused the interaction between PVA and inorganic layers. The composites showed different fine stable thermal properties and dynamic mechanical properties and photo-degradable properties with those of PVA alone.



Scheme 1 Photodegradation of PVA

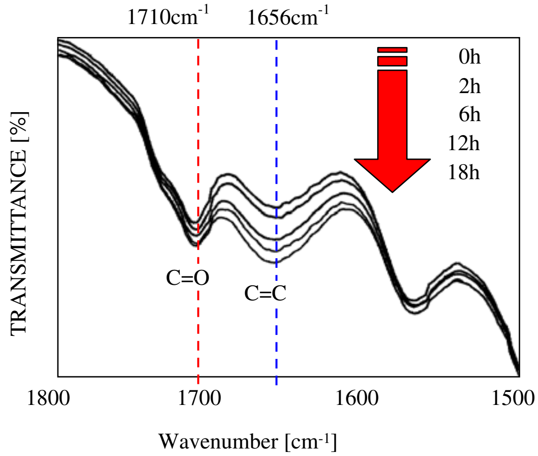


Fig. 5 FTIR spectra of PVA film before and after UV irradiation

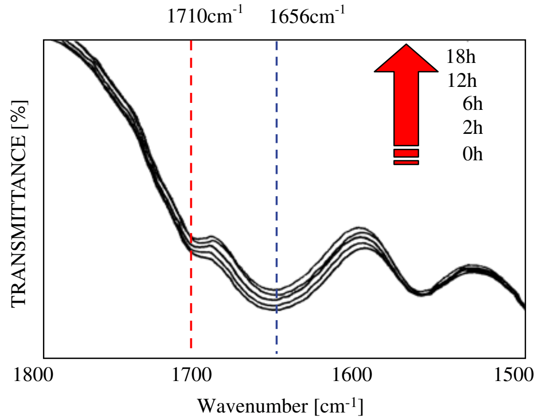


Fig. 6 FTIR spectra of OMMT/ PVA (1 wt.%) film before and after UV irradiation

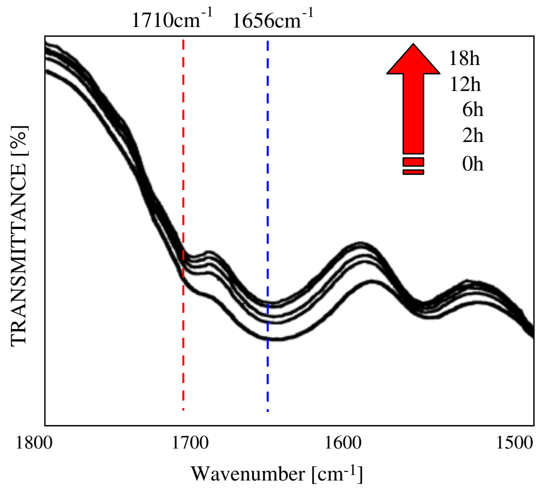


Fig. 7 FTIR spectra of perlite/PVA (1 wt.%) film before and after UV irradiation

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