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UV curable transparent urethane-acrylate/clay nanocomposite coating materials with thermal barrier property

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ABSTRACT

The incorporation of organically modified montmorillonite (MMT) as thermal barriers into an UV curable urethane-acrylate based resin system was attempted to prepare nanocomposite coating materials with improved thermal barrier property using a two-step solution mixing process. The prepared nanocomposite sols were deposited on glass substrates using a bar coating method, and cured under radiation. We explored the correlation between the mixing time in association with shear stress imposed on clay agglomerates, and the resulting nanostructured morphology including the degree of exfoliation and dispersion state of the clay in the prepared nanocomposites. The effects of the nanoclay loading level on the properties and morphology of the nanocomposites were also investigated. As a result, it was revealed that with an appropriate level of clay loading at 5 wt.% and shear stress, high degree of intercalation and exfoliation structure with homogeneous clay dispersion in the matrix could be achieved, and for the nanocomposite-coated glass, the thermal barrier performance was noticeably enhanced by 72% over that of non-coated glass, while exhibiting fairly good optical transparency with light transmittance over 80%. In addition, the thermal stability and dynamic mechanical properties of the nanocomposites were also improved. It can be anticipated that a novel method for preparing the UV curable nanocomposite coatings on glass, which is presented in this study, will be utilized to fabricate the thermally insulated transparent window system.

1. Introduction

In recent decades, the total area covered by glass windows in buildings or houses has been increasing to allow for sufficient daylight transmittance and better view, which has caused an increase in energy consumption because most energy loss in buildings occurs through the windows. Therefore, the need for the development of a thermally insulated transparent window system, which is the most significant part in the construction of energy-efficient buildings, has consistently been increasing, in order to save energy costs and to minimize carbon dioxide emissions by reducing the use of carbonaceous fuel [1].

Currently, multi-layered glass, in which the volume between glass plates is filled with air or evacuated, has been widely used commercially for window systems in buildings for the purpose of thermal insulation and sound proofing. However, this window system has drawbacks of high costs of installation and the product itself. Accordingly, glass windows with a coating layer have drawn much attention because they are advantageous over window systems with multi-layered glass with regard to both constructability and economics.

Silica aerogels with nano-sized open pores, have extraordinary properties such as high porosities, high specific area, and very low thermal conductivity, and have recently been used to fabricate thermally insulated transparent windows [2,3]. Window glazing coated with in-situ synthesized silica aerogel film has exhibited excellent thermal barrier property [4,5], but it still has technical problems to overcome for practical application in building construction because the silica aerogel coating layer has low elasticity and poor adhesion to the glass substrate. Therefore, we have attempted to incorporate powdery silica aerogel into ultra-violet (UV) curable acrylate resin to prepare hybrid coating materials with thermal barrier property, for application to glass windows [6]. However, this coating material has also revealed a limitation in the appreciable improvement of thermal barrier property, which might be due to partial pore collapse of the silica aerogel induced by the penetration of oligomeric resin molecules into open pores during the mixing process. In addition to silica aerogels, various inorganic powdery materials with high resistance to heat transfer, such as hollow micro-beads of silica and glass, and nanoparticles of Al-doped ZnO and antimony-doped tin oxide (ATO), have been used to prepare organic/inorganic hybrid coatings on glass with thermal barrier performance [7–12].

In the present work, we attempted the preparation of UV curable urethane-acrylate based nanocomposite coating materials with improved thermal barrier property using nanoclays as thermal insulators.

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Inorganic nanoclay has been widely used to enhance the physical properties of the polymers, including thermal, mechanical, and heat/gas barrier properties [13–18]. It can be expected that nanoclay platelets with very high aspect ratio, dispersed in the polymer matrix, increase the resistance to thermal transfer through polymer nanocomposites by increasing the tortuous pathway for thermal transfer. To date, there have been no reports in the literature for thermally insulated glass coatings prepared by incorporation of nanoclays into polymers. Using X-ray diffraction (XRD) analysis and transmission electron microscope (TEM) observation, we investigated the nanostructured morphology including the dispersion state and intercalated/exfoliated structure of the nanoclays in the prepared nanocomposites. The optical transparencies and thermal barrier properties of the coated glasses were evaluated as a function of added nanoclay content in the poly(urethane-acrylate)/clay nanocomposites, and the mechanical property, thermal stability were also discussed to present a reinforcing effect caused by incorporation of nanoclays.

2. Experimental

2.1. Materials

Organically modified montmorillonite (MMT) nanoclay used in this study was purchased from Southern Clay Products with the commercial name of Cloisite 30B (C30B, CEC (cation exchange capacity): 90 meq/100 g), which is modified with a quaternary ammonium salt containing one methyl, one tallow, and two hydroxyethyl groups. As the organic binder resin, the UV curable acrylic resin system is composed of aliphatic urethane hexaacrylate (UP118, SK Cytec) and two different reactive diluting acrylates with various multi functional groups: trimethylolpropane triacrylate (TMPTA, Aldrich), 1,6-haxanediol diacrylate (HDODA, Aldrich). 1-Hydroxy-cyclohexyl-phenyl-ketone (IRGACURE 184, Ciba Specialty Chemicals) was used as a photoinitiator.

2.2. Preparation of nanocomposites and coated glasses

The organic UV curable resin system was prepared by mixing 3 different acrylic oligomers based on a composition of 50 wt.% of UA118, 20 wt.% of TMPTA, 30 wt.% of HDODA, and then combining with 5 phr of photoinitiator. To obtain uncured nanocomposite coating sols with sufficiently exfoliated clay dispersion, this acrylic resin system was mixed with nanoclays via two-step mixing process assisted by a sonicator (ULH 700S, Ulssohitech Co.) and a homogenizer (MD 600, Esyndmt Co.). The mixture was sonicated for 30 min followed by mixed vigorously for another 30 min with the homogenizer at room temperature. The incorporated clay contents were adjusted to 3, 5, 8, and 12 wt.% in preparation of the poly(urethane-acrylate)/clay nanocomposites. The prepared nanocomposite sols were deposited on the glass substrates with a thickness of 90 μm using a bar coater (RDS #12, Webster). The coated glasses were cured in a batch-type UV curing system (Unilam Co.) equipped with a UV-lamp (MFUV-01L21) with irradiation intensity of 120 mW/cm^2. For the characterization of morphology, thermal and mechanical properties, nanocomposite sheet samples were also obtained in addition to the preparation of the coated glasses by casting of nanocomposite solutions onto polyimide film followed by UV curing. All of the cured samples were kept in a dessicator to prevent the influence of moisture prior to performing the characterization.

2.3. Characterization

The gallery distance in the clay intercalated by oligomeric urethane-acrylate molecules during the vigorous two-step mixing process was quantitatively measured on an X-ray diffractometer (Ultima III, RIGAKU, Japan) with Cu Kα radiation operated at 40 kV and 150 mA. Samples were scanned in the range of 1–10° at a scanning rate of 1.0°/min. The analysis of the cured nanocomposite was carried out in the form of a sheet, while the pristine clay was analyzed in the powder form. The basal spacing of the clay was determined from the position of the d_{001} peak in the X-ray diffraction (XRD) pattern using Bragg's law. The clay dispersion state in the nanocomposites was qualitatively observed using a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) at an accelerating voltage of 200 kV. The specimens were prepared for TEM observation with a thickness of about 100 nm by ultramicrotoming the cured epoxies containing the nanocomposite sheet with a diamond knife.

Thermogravimetric analysis of the poly(urethane-acrylate)/clay nanocomposite was performed with an Exstar 7300 instrument (Seiko, Japan) at a heating rate of 10 °C/min in the temperature range of 25–700 °C. The dynamic viscoelastic properties of the nanocomposite materials were measured using a dynamic mechanical analyzer (Exstar 6000, Seiko, Japan) with a strain amplitude of 0.5% at a frequency of 1 Hz. The temperature was increased from room temperature to 180 °C with a heating rate of 2 °C/min. The optical transmittance of the coated glass was measured using a visible spectrometer (Optizen 1412V, Mecasys Co.) in the visible-light wavelength range of 350–850 nm. The thermal barrier property of the coated glass was evaluated using a thermal conductivity analyzer (LFA457, Netzsch Co.) based on the laser flash analysis (LFA) method according to ASTM E1461.

3. Results and discussion

3.1. Clay dispersion in nanocomposites

For the preparation of high-performance polymer nanocomposites, one of the significant variables is to achieve a homogeneous and uniform dispersion structure of intercalated or exfoliated nanoclay platelets in the polymer matrix [14]. In this study, the clay dispersion state in the prepared poly(urethane-acrylate)/clay nanocomposite was examined using XRD analysis and TEM observation as quantitative and qualitative methods, respectively. Fig. 1 shows the XRD patterns of the pristine C30B clay and corresponding nanocomposites with different clay loadings in the 2θ range of 1–10°. The diffraction peak of the pristine C30B is shown at 2θ = 4.8°, which corresponds to an interlayer basal (d_{001}) spacing of 1.84 nm. For the prepared nanocomposites with clay loadings of 3, 5, and 8 wt.%, this peak disappears and no peaks are observed, indicating the formation of fully exfoliated structure leading to good clay dispersion in the acrylate matrix. It can also be deduced from disappearance of these peaks that in addition to the fully exfoliated nanoclay platelets, which are mostly occupied in the whole matrix, there are some intercalated silicate layers with gallery distance larger than 6–7 nm corresponding to allowable minimum angle in the investigated range of 2θ. In addition, such a flat diffraction pattern without peak may originate from various factors such as layer

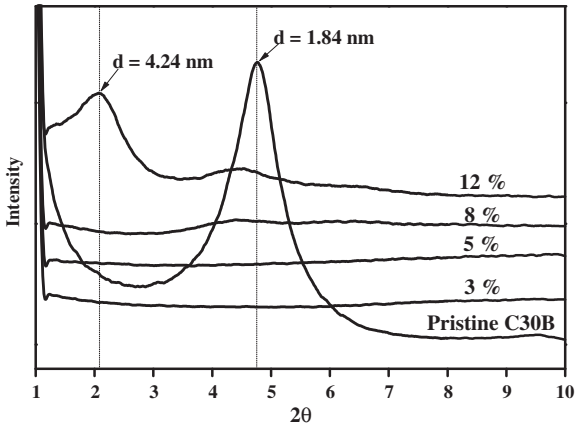

Fig. 1. XRD patterns of pristine C30B and poly(urethane-acrylate)/clay nanocomposites with various clay contents.

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