



# Preparation and properties of hydrophobic layered silicate-reinforced UV-curable poly(urethane acrylate) nanocomposite films for packaging applications



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## ABSTRACT

A series of poly(urethane acrylate)/Cloisite 15A (PUA/C15A) nanocomposite films were successfully prepared via a UV-curing system, and their physical and barrier properties were investigated as a function of clay content. The physical properties were strongly dependent upon the chemical and morphological structures originating from differences in Cloisite 15A content. With high clay content, the PUA/C15A nanocomposite films displayed an intercalation/exfoliation combined structure. However, no strong interfacial interactions occurred between the PUA and clay, possibly leading to poor dispersion with relatively high clay content. The thermal stability displayed some enhancement with the introduction of clay into PUA, while the gas and moisture barrier properties showed significant enhancement. The oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) decreased with increasing contents of Cloisite 15A, and varied within the range of 714.0–71.1 cm<sup>3</sup>/m<sup>2</sup> day and 29.9–13.9 g/m<sup>2</sup> day, respectively. Thus the enhanced gas and moisture barrier properties of PUA/C15A nanocomposite films make them promising candidates for food and pharmaceutical packaging applications. However, further studies will be performed to increase the compatibility and dispersion of clay particles in the PUA polymer matrix.

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## 1. Introduction

Growing concerns for environmental protection have driven industry toward the use of solvent-free polymerization systems, where ultraviolet (UV)-curing has become a viable alternative to conventional thermal curing of solvent-containing polymer formulations. Added benefits of UV-curable materials such as fast curing speed, low energy consumption, high cost efficiency, and less pollution have led to their increased use in various industries, where applications include paints, thin film coatings, adhesives, packaging overcoat films, and biomedical materials [1–3]. Low viscosity and high curing speed are two desirable properties pursued by industry for UV-curable oligomers. Of the UV-curable polymers, poly(urethane acrylate) (PUA) is one of the most widely used polymers due to its high solubility, low melting viscosity and three-

dimensional architectures, though efforts to improve properties and expand applications in various areas continues [3,4]. Despite these advantageous properties, issues related to low barrier and mechanical properties remain when applying PUA films to food and pharmaceutical packagings [5,6].

In the food and pharmaceutical packaging industries, good gas and moisture barrier properties are critical for achieving a long protective period for packaged products [7,8]. The reduction of oxygen, moisture sorption, and diffusion can suppress internal damage and improve long-term performance. Therefore, barrier films must prevent or at least decrease the gas/moisture transfer between the product and the surrounding atmosphere. Recently, the combination of organic polymers and inorganic fillers has become an exciting subject, receiving considerable research attention for the improved thermal stability, mechanical strength, vapor permeability, and optical and electrical properties created by the organic–inorganic hybrid materials [1,2,4,9–12]. To achieve enhanced physical properties and processability in the inorganic–organic hybrid materials, it is necessary to homogeneously disperse inorganic filler into the organic polymer matrix [1,3,9–11].

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There have been some studies on UV-curable polymer/clay nanocomposites [1,2,4,9,13]; however, most have focused on the improvement of physical properties of the nanocomposites, such as thermal and mechanical properties. To expand the use of UV-curable PUA into food and pharmaceutical packaging industries, improvements in the gas and moisture barrier properties of films are essential factors in addition to thermal and mechanical properties [10,11].

In this study, a commercially available, organically modified, layered silicate with a relatively high hydrophobic surface, Cloisite 15A [14,15], was selected, and poly(urethane acrylate)/Cloisite 15A (PUA/C15A) nanocomposite films were prepared with 0, 0.5, 1, 3 and 5 wt% clay loadings. As a reactive monomer, methyl methacrylate (MMA), having high dipole moment value, was used to enhance dispersion and exfoliation of Cloisite 15A in PUA matrix. Chemical structures were confirmed via Fourier-transform infrared (FT-IR) spectrum, while the morphologies were corroborated via X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM). Further effects of organoclay on thermal and mechanical properties have been studied on the basis of thermal gravimetric analyzer (TGA), differential scanning calorimeter (DSC), and nanoindentation. The barrier properties of the as-prepared nanocomposite films were investigated by measuring the oxygen transmission rate (OTR) and the water vapor transmission rate (WVTR), and were interpreted by relating to the chemical structure and morphology of the films.

## 2. Experimental

### 2.1. Materials

Polycaprolactone triol (PCLT, average Mn: 900 g/mol, CAS No: 37625-56-2) as a polyol, 2-hydroxyethyl acrylate (HEA, Mw: 116.12 g/mol, CAS No: 37625-56-2) as a reactive monomer, and dibutyltin dilaurate (DBT, Mw: 631.56 g/mol, CAS No: 77-58-7) as a reaction catalyst were purchased from Aldrich Chemical Co. Isophorone diisocyanate (IPDI, Mw: 222.28 g/mol, CAS No: 4098-71-9) as a diisocyanate was purchased from TCI Korea. Trimethylolpropane triacrylate (TMPTA, Mw: 296.32 g/mol, CAS No: 15625-89-5) and methyl methacrylate (MMA, Mw: 100.12 g/mol, CAS No: 80-62-6) as reactive diluents were purchased from Miwon Commercial Co. Ltd (Anyang City, Korea) and Aldrich Chemical Co., respectively. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184D, Mw: 204.26 g/mol, CAS No: 947-19-3) as a photoinitiator was purchased from Ciba Specialty Chemicals Co. Cloisite 15A (CAS No: 68953-58-2), a natural montmorillonite modified with a dimethyl dehydrogenated quaternary ammonium salt with an interlayer spacing of 21.5 Å, was kindly supplied from Southern Clay Products Inc. All the chemicals were of reagent grade and used without further purification.

### 2.2. Preparation of urethane acrylate oligomer and PUA/C15A nanocomposite films

Our method for preparing crosslinkable urethane acrylate oligomer PCLT-IPDI was described in our previous studies [10–12]; PCLT and IPDI (1:2.5 by mole) were mixed in a 500 mL four-necked flask in an oil bath equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser with a drying tube, and thoroughly mixed. Approximately 200 ppm of DBT was then added. After the urethane-forming reaction proceeded at 80 °C for over 3 h, the reaction mixture was cooled to 60 °C, and HEA was added dropwise. Tipping the NCO-terminated prepolymer with HEA was done for 1 h at a temperature below 60 °C.

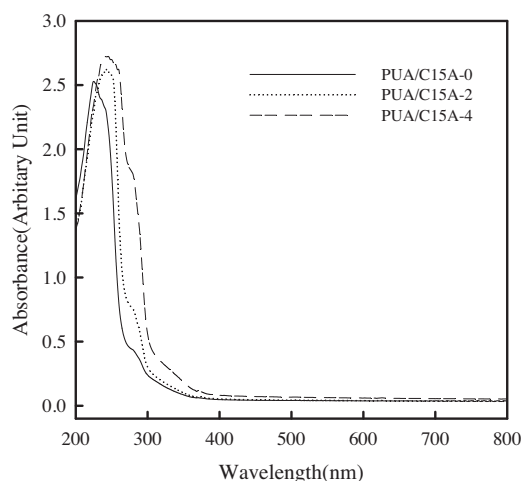


Fig. 1. UV-vis absorbance spectra of the PUA/C15A nanocomposite films.

Cloisite 15A was first dispersed in MMA using a magnetic stirrer and ultrasonic cleaner for 24 h [16,17]. And then, the MMA and clay dispersion, urethane acrylate oligomer and TMPTA were put into the vial glass and the mixture solution was sonicated using an ultrasonicator (Ultra-cell Vcx 750, power: 750 W; frequency: 20 kHz) for 4 h. Finally, the oligomer and photoinitiator were put into the mixture solution and stirred with ultrasonication for 0.5 h. Each mixture solution was then bar-coated on a glass substrate. The coated films were exposed to UV irradiation from a medium-pressure 1.2 kW mercury lamp (main wavelength: 365 nm) for 10 min. The film thickness was kept at approximately 30 μm to aid in the evaluation of physical properties. The clay loadings in the nanocomposites were 0 wt%, 0.5 wt%, 1 wt%, 3 wt%, and 5 wt%, respectively, and the compositions and sample codes for the nanocomposite films are summarized in Table 1. Fig. 1 shows the UV-vis absorbance spectra of the PUA/C15A nanocomposite films. Although the absorbance slightly increases with increasing clay content, the difference of absorbance at the main wavelength of 365 nm is not big, which indicates that the clay incorporation does not affect the degree of photopolymerization by our UV curing.

### 2.3. Characterization

FTIR spectra of the as-prepared PUA/C15A nanocomposite films were recorded with a Spectrum 65 FTIR spectrometer in attenuated total reflection (ATR) mode (PerkinElmer Co. Ltd., Massachusetts, USA). X-ray diffraction (XRD) was used to identify the dispersed state over a fairly large sample volume. In this study, XRD patterns were collected on a Siemens Bruker-AXS D5005 diffractometer with a nickel-filtered CuKα radiation source ( $\lambda = 1.5418 \text{ \AA}$ ). The radiation source was operated at 40 kV and 45 mA, and data were collected in the  $2\theta$  range from 1° to 9° at 0.02° intervals, and with a scan speed of 2.0°/min.

The fractured surfaces of the PUA/C15A nanocomposite films were investigated using a Quanta 250 SEM (FEI Co. Ltd., Hillsboro, OR, USA). Prior to the examination, all of the samples were coated with a thin layer of platinum (Pt). The morphology of the PUA/C15A nanocomposite films was also examined via TEM with a Hitachi electron microscope. The samples for the TEM analysis were sectioned with an ultramicrotome.

The decomposition temperature and thermal behaviors of the PUA/C15A nanocomposite films were investigated by using a Q10 differential scanning calorimeter (TA Instrument Co. Ltd., Delaware, USA) and a TGA 4000 thermogravimetric analyzer (PerkinElmer Co.

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