Synthesis of epoxy encapsulated organoclay nanocomposite latex via phase inversion emulsification and its gas barrier property

Viet Hung Pham [a], Yong Woo Ha [a], Sang Hun Kim [b], Ha Taek Jeong [b], Man Yong Jung [b], Bong Seong Ko [b], Young Jun Hwang [b], Jin Suk Chung [a],*

[a] School of Chemical Engineering & Bioengineering, University of Ulsan, Ulsan 680-749, Republic of Korea
[b] KCC Corporation, Central Research Institute, Mabookdong 83, Yonginsi, Gyunggido 446-716, Republic of Korea

ARTICLE INFO

ABSTRACT

Waterborne epoxy–clay nanocomposites were prepared by encapsulation of organoclays in epoxy latex particles via phase inversion emulsification. The organoclays were exfoliated in the epoxy backbone before compounding with a hardener and subsequently dispersing in water. The encapsulation of clay platelets into the waterborne epoxy latex particle resulted in an exponential increase in particle size, from 5 to 10 times at a clay loading of only 1–2 wt%, respectively. The XRD patterns and TEM images show that clay platelets were well intercalated and exfoliated in the epoxy matrix. The gas barrier performance of the epoxy–clay nanocomposite strongly depended on the kind of organoclay. The best oxygen barrier efficiency was approximately 14% at 2 wt% clay loading.

© 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

With environmental criteria becoming stricter, waterborne coatings have been gaining importance in the modern coating industry [1–3]. Compared to their solvent-based counterparts, waterborne coatings offer advantages of lower levels of volatile organic compounds (VOCs), odor, flammability and a higher level of safety. Epoxy resin is one of the most important materials in the coating industry due to its outstanding performance in corrosion protection and chemical resistance [4–7]. An effective method to prevent corrosion is to improve the barrier property of the coatings to decrease the permeability of water and oxygen, which fuel the corrosion process [5,8]. Clay, a plate-like layered silicate, is well-known effective nanofiller that improve the gas barrier performance of various polymers, including epoxy coatings [9–14]. By incorporating the clay into the polymer matrix, the permeating molecules (oxygen, nitrogen, carbon dioxide, water and hydrocarbons) are forced to randomly migrate around the clay platelets, diffusing through a tortuous pathway [9,11,12]. The reduction in permeability strongly depends on the aspect ratio of the clay platelets, where high ratios dramatically enhance gaseous barrier properties. The best gas barrier properties would be obtained in polymer nanocomposites with fully exfoliated clay platelets [11,12]. Numerous papers investigating the preparation of solventborne epoxy–clay nanocomposites and their properties, such as thermal, mechanical and gas barrier have been published [15–22]. However, waterborne epoxy–clay nanocomposite has not been thoroughly studied yet [23].

Waterborne epoxy resins are the principal binder component of modern cationic electrocoat paints which offer outstanding anticorrosion protection even in very thin films and are extremely eco-efficient since they contain virtually no solvents. The epoxy resins for these cationic electrocoat paints are polyaddition products of epichlorhydrin and bisphenols, which have molecular weights of approximately 400–4000 g mol^{-1} and 1–2 epoxy terminal groups per molecule. Epoxy and hydroxyl groups of epoxy resin must be chemically modified by primary or secondary amines into tertiary amino groups, followed by neutralized with low-molecular carboxylic acids to yield water-dispersible products [5]. In comparison to solventborne epoxy counterpart, waterborne epoxy is much more hydrophilic. Therefore, in preparation of waterborne epoxy–clay nanocomposite, to have high compatibility between nanofiller and epoxy matrix, organoclay must be highly hydrophilic. In this study, we prepared waterborne epoxy–clay nanocomposites by encapsulation of organoclays into waterborne epoxy latex particles by phase inversed emulsification to improve the oxygen barrier property of waterborne epoxy resin. Two kinds of highly hydrophilic organoclays including commercial organoclay Cloisite 30B (Southern Clay Product Inc., USA) and natural clay modified by short alkyl ammonium salt were used to prepare

---

composite. The oxygen barrier efficiency of waterborne epoxy–clay composites gradually increased with clay loading, up to 14% at 2 wt% of clay.

2. Experimental

2.1. Materials

Epoxy resin Epokukdo YD-128 was purchased from Kukdo Chemical. Benzyl chloride, di(butylamino) ethanol, butyl carbitol, 1-methoxy-2-propanol (MOP), N-methyl ethanolamine, diketimine, methyl isobutyl ketone (MIBK), and methylene diphenyl diisocyanate (MDI) (Sigma Aldrich Co.) were used without further purification. Commercial grade organoclay Cloisite 30B and natural clay Cloisite® Na+ were kindly provided (Southern Clay Product Inc., USA).

2.2. Organo-modification of natural clay

The organo-modifier was synthesized by the following procedure [15]. Benzyl chloride (0.105 mol) was slowly added to 50 mL solution of di(butylamino) ethanol (2 M) in ethanol, and the mixture was stirred overnight under reflux. The product was purified by extracting twice with ether after evaporating the ethanol. The obtained quaternary ammonium salt was recrystallized in acetone and denoted as Bz1OH.

An 8 g sample of natural clay (Cloisite® Na+) was stirred in 500 mL of deionized water at 70 °C for 5 h, and then 200 mL of ethanol was added. The clay was dispersed by sonication for 10 min. To this dispersion, a solution of 4.64 g of Bz1OH, corresponding to 150% cation exchange capacity (CEC) of natural clay (CEC ~ 92 mequiv./100 g clay), in 100 mL of ethanol was added dropwise (within 2 h) under stirring. The reaction mixture was stirred overnight at 70 °C, and the product was filtered and washed with a hot water–ethanol mixture (1:1), hot ethanol and then MOP. The obtained product was denoted as Bz1OH-m-clay.

2.3. Preparation of waterborne epoxy–clay nanocomposite by phase inversion emulsification

Cloisite 30B and Bz1OH-m-clay were dispersed in MOP by sonication for 30 min to create MOP-clay suspensions. 300 g of epoxy resin and 100 g of MOP were consecutively charged into a 4-neck reactor. The mixture was mixed at 200 rpm, and the temperature was increased to 110 °C for 30 min. Then, 40 g of diketimine and 30 g of methyl ethanolamine was added and mixed for 2 h. Finally, 250 g of MOP-clay suspension with the predetermined clay loading were added and mixed for 2 h.

350 g of the epoxy resin backbone–clay suspension and 150 g of hardener were charged into the reactor, mixed at 200 rpm, and the temperature was increased to 90 °C and held for 30 min. Approximately 150 g of solvent was recovered via vacuum application. Next, 5.3 g of formic acid was added to neutralize the unreacted amine groups, the temperature was adjusted to 75 °C and 250 g of deionized water was slowly added under mixing to create a water-in-epoxy resin emulsion. The temperature was adjusted to 55 °C, and 400 g of deionized water was continuously added. During water addition, an increase in the dispersed phase in the water-in-epoxy resin emulsion resulted in phase inversion to form an epoxy resin-in-water emulsion. The epoxy–clay nanocomposite latex had a solid content of approximately 35 wt%.

2.4. Characterizations

The size of epoxy–clay nanocomposite latex particles was measured by dynamic light scattering (Mirotrac S3500). The thermal properties of organo-modified clays were determined by thermal gravimetric analysis (TGA TA Q50) at a scan rate of 10 °C/min in air. The effect of natural clay organo-modification and the exfoliation of clay platelets in the epoxy matrix were characterized by a high power X-ray diffractometer (D/MAZX 2500 V/PC, Rigaku) with Cu Ka radiation (35 kV, 20 mA, λ = 1.5418 Å) at a scan rate of 2° (2θ) min⁻¹. The encapsulation of the clay platelets in the epoxy latex particles was characterized by a transmission electron microscope (TEM, JEOL JEM 2100). The sample for TEM characterization was prepared by dropping diluted waterborne epoxy–clay nanocomposite latex on TEM grid, followed by drying at room temperature in vacuum.

To characterize the oxygen permeability of the waterborne epoxy resin–clay nanocomposite, the epoxy–clay nanocomposite latex was cast onto corona-treated polyester film by an automatic film-coating apparatus (Comate 3000V, IRAE) and dried in air for 2 h before curing at 165 °C for 2 h. The oxygen transmission rate through the polyester film coated with the pristine epoxy and epoxy–clay nanocomposite was measured using a gas permeability analyzer (Yanco GTR-10). The total transmission rate (T_{tot}) of oxygen was normalized with respect to the total thickness (t_{tot}), and the transmission rate through the pristine epoxy or epoxy–clay nanocomposite films was calculated as follows:

$$\frac{t_{tot}}{T_{tot}} = \frac{t_1}{T_1} + \frac{t_2}{T_2}$$

where t_i is the thicknesses of the coated film and polyester film, and T_i is the corresponding normalized transmission rate.

3. Results and discussion

3.1. Organo-modification of natural clay

The commercial organoclay Cloisite 30B, the most hydrophilic organoclay in the commercial Cloisite series [24], is widely used as nanofiller to improve the mechanical and thermal properties of epoxy nanocomposites due to its high compatibility [16,17,19,20]. However, Osman et al. [14] studied the effect of organo-modified clay on the gas permeability of solventborne epoxy–clay nanocomposites and reported that a long alkyl chain organo-modifier enhanced the polymer intercalation into clay galleries but increased the permeability coefficient, likely due to phase separation at the interface between the epoxy matrix and clay platelets. The clay modified with short alkyl ammonium salt exhibited better oxygen barrier performance. In this study, Cloisite 30B and natural clay modified with benzyl dibutyl hydroxyl-ethyl ammonium salt (Bz1OH) were used to study oxygen barrier property of waterborne epoxy–clay nanocomposite.

The efficiency of organo-modification of natural clay with Bz1OH was determined by TGA in an air atmosphere (Fig. 1a). The TGA thermograms show that the residue of Bz1OH-m-clay at 900 °C were approximately 77.1%, corresponding to a cation exchange efficiency of 91.6 mequiv. or a clay modification efficiency of 99.6%. The XRD pattern of natural clay (Fig. 1b) exhibited d-spacing peaks near 7.3°, corresponding to an interlayer spacing of approximately 11.9 Å. After modification with Bz1OH, the d-spacing peak of natural clay shifted to smaller angles at 5.6°, corresponding to interlayer spacing of 15.7 Å. In comparison with Cloisite 30B (interlayer spacing ~ 19.7 Å), the interlayer spacing of Bz1OH-m-clay was slightly smaller due to the smaller size of ammonium salt.