

Tetra-*n*-butylammonium Salt로 개질된 Montmorillonite Nanoplatelet를 이용한 에폭시 수지의 환경 내구성 개선

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Improving Environmental Durability of Epoxy Resin Using Tetra-*n*-butylammonium (TBA) Salt Modified Montmorillonite Nanoplatelets

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Abstract: This study aimed to investigate the effect of organoclay concentration variation (1-5 wt%) on the weathering resistance of epoxy resin in terms of the strength, modulus and weight changes of the specimens after exposure to accelerated weathering conditions. Transmission electron microscopy (TEM) revealed an exfoliated and good dispersed nanofiller structure throughout the matrix up to 3 wt% loading. The tensile strength, modulus, and weight of the samples decreased after combined UV radiation and condensation, with much less extent for the nanocomposites than neat epoxy indicating that the presence of organoclay led to dominant enhancement in mechanical properties endurance of epoxy resin to environmental degradation. Nanocomposites also displayed much lower weight loss as compared to the unfilled epoxy after being subjected to the accelerated weathering by either temperature-humidity or by combined UV radiation and condensation.

Keywords: nanocomposites, epoxy, organoclay, accelerated weathering, mechanical properties.

Introduction

Epoxy resins are considered to be the most important class of thermoset polymers due to their excellent strength, chemical resistance, and electrical properties. They have found remarkable applications as bonding agents and adhesives, protective coatings, electrical laminates, apparel finishes, flooring and paving, and high performance composites.^{1,2} Despite their

inherent advantages, they are susceptible to the environmental conditions primarily due to the degradation of the epoxy matrix. Hence, there are concerns regarding their overall long-term durability, especially as related to the capacity for sustained performance under harsh and changing environmental conditions. During last two decades many researchers have focused on the increasing environmental durability of the epoxy based polymers. Using durable top coats, UV stabilizers, impact modifiers are some examples.² Whereas, the inclusion of nanofillers in the epoxy based matrixes is an effective and promising method to overcome these drawbacks.³⁻⁶

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In recent years, polymer/clay nanocomposites have attracted great attention in both academic and industrial researches, due to their synergistic advanced properties at relatively low nanoclay loadings (up to 5 wt%).⁷⁻¹² The typical enhanced properties include tensile strength, heat deflection temperature, barrier properties, and so on.¹³⁻¹⁵ Because of these good properties and low price, industrial applications of nanoclay also found great attraction nowadays. One of good examples is clay/nylon 6 nanocomposites developed by Toyota group with excellent mechanical properties.¹⁶

There are two important challenges in the dispersion and distribution of nanofillers in polymer systems during the preparation of nanocomposites, which mostly originate from nature of the nanoscale; first, the separation of nanoparticles with high surface tension, and the second, the interaction between nanoparticles and matrix. During last two decades, several methods have been developed to modify nanoclays, such as ion exchange modifiers, ring opening coupling agents and silane coupling agents.¹⁷⁻¹⁹

In this study, sodium ions between the nanoclay layers were replaced with a cationic modifier, Tetra (*t*-butyl ammonium), to improve the dispersion of clay nanoplatelets in epoxy resin.²⁰ Afterward, epoxy based nanocomposites containing 1-5 wt% modified nanoclay were prepared, and the effects of two different accelerated environments on their endurance were investigated.

Experimental

Materials. Nanoclay (Na-MMT) with an ion exchange capacity of 115 meq/100 g was purchased from Kurimine Industries, Japan. Tetrabutylammonium chloride (TBA, purity $\geq 97.0\%$) was obtained from Sigma-Aldrich Co., USA. Epoxy resin based on diglycidyl ether of bisphenole A (EPO 5019, AXSON Technologies US, Inc.) and an aliphatic polyamine curing agent (Aradur[®] 956-2, Huntsman Advanced Materials, USA) were used as received.

Modification of Nanoclay and Preparation of Nanocomposites. Desired amount of nanoclay was first poured in distilled water and stirred for 2 h, Tetra was then added to the mixture and stirred for more 30 min. Then, the obtained dispersion was sonicated (HF-GM 2200 sonicator) for 30 min, and subsequently stirred at 80 °C for more 4 h. Finally, the modified nanoparticles were filtered and washed 4 times and dried in a vacuum oven at 100 °C for 12 h.

In sake of good dispersion and exfoliation of the modified

nanoclay nanoparticles in the matrix, combination of mechanical mixing, sonication and high-shear dispersion processes were used.^{21,22} The neat epoxy sample was prepared by mechanical mixing of the resin and curing agent for 10 min. Then, the mixture was degassed in a vacuum oven for 1 h before being poured into a teflon-coated stainless steel mold. Curing process was conducted at 80 °C for 24 h, followed by postcuring at 120 °C for 8 h. The epoxy/modified-nanoclay composites were fabricated in three steps; first, a desired amount of clay (1-5 wt%) was added to the liquid epoxy resin (preheated to 50 °C) and mechanically stirred for 12 h. The obtained mixture then was subjected to ultrasonic pulses for 30 min. Subsequently, it was processed in a high-speed shear homogenizer operating at 12000rpm for 30 min. The sonication and high-shear process produce heat due to frictional dissipation in the polymer system, hence the temperature of the mixture was maintained at 50 °C using a water bath. The mixture was then degassed in a vacuum oven for 2 h to remove any trapped air. Desired amount of the curing agent was then added to the mixture and mixed gently to avoid introduction of any air bubbles. Finally, the mixture was poured into a teflon-coated stainless steel mold and allowed to cure at 80 °C for 24 h, followed by postcuring at 120 °C for 8 h.

Accelerated Weathering Tests. The samples were subjected to two different accelerated environment for evaluating their environmental durability. During the first accelerated environment (designated as UWT), the samples were exposed to combined UV radiation and condensation, according to "ASTM G 154 standard practice in a QUV chamber (Model QUV/Spray, Q-Panel Co.) for 4800 h. As the samples were alternately exposed to UVB radiation (313 nm, 0.71 W m⁻²) at a temperature of 60 °C for 4 h and followed by 4 h of water condensation at a temperature of 50 °C cyclically.

In the second accelerated environment test (designated as WT), a constant 80% relative humidity condition at 50 °C was applied to the samples in a temperature-humidity chamber. Four samples were used for each batch condition, and three samples were kept as reference. For the first two weeks the samples were weighed every 24 h. Afterwards, the samples were weighed every 48 h and finally every 72 h. The samples were taken out from the machine and the weight of the samples was recorded after drying.

Moreover, for evaluation of the effect of accelerated weathering on samples, weight loss at a time of t (ΔW_t) was calculated with following equation:

$$\Delta W_t(\%) = \left[\frac{W_0 - W_t}{W_0} \right] \times 100 \quad (1)$$

where W_t and W_0 are weight of the reference sample at $t=0$ and weight of the sample at a time of t , respectively.

Characterization. Modification of clay nanoparticles was investigated using a Fourier transform infrared spectroscopy (FTIR) apparatus (IFS48 Bruker, Germany) with 16 scan per sample cycle, and thermogravimetric analyzer (TGA, PL-1500, England) under N_2 atmosphere from room temperature to 600 °C with a heating rate of 10 °C/min. The micrographs were obtained using an EM-208S Philips transmission electron microscope (TEM). Mechanical properties of samples were measured on a universal testing machine (Instron 6025, England) according to ASTM D638. All mechanical tests were conducted at a strain rate of 5 mm/min. Tensile properties of at least five specimens were determined for each sample, and the average was reported.

Results and Discussion

FTIR Spectroscopy. The modification of nanoclay was investigated by FTIR and thermogravimetric analysis (TGA) techniques. FTIR spectra of primary and modified nanoclay are represented in Figure 1(a). As it can be seen, after modification of nanoclay with Tetra, new peaks were appeared in the ranges of 2700–2960 and 1340–1475 cm^{-1} in the spectrum modified clay, which can be correlated to the stretching and bending vibration of alkyl groups of organic modifier, respectively. Since the residual (non-reacted) modifier has been washed, these peaks exhibit that surface modification of the

nano-particles has occurred successfully.

TGA. TGA thermograms of the as received nanoclay, alkyl ammonium and organoclay are shown in Figure 1 (b). The weight loss between 40 and 100 °C is probably due to desorption of physisorbed water. As can be seen from Figure 1(b), the modified clay nanoparticles show sharp weight loss, beginning near 210 °C, continues till 350 °C, which can be attributed to a large scale thermal decomposition of Tetra chains.²³ On the other hand, TGA can be a useful tool to estimate the amount of the organic grafted substances onto the nanoclay minerals, because these materials can be thermally degrade in a temperature range of 200–500 °C. Hence, by subtracting weight loss of the pristine clay from weight loss of the modified clay at 600 °C, the proper weight loss (originated exclusively from Tetra) was obtained 15.4%.

TEM. TEM was used to investigate the dispersion state of nanoclay in epoxy resin. Figure 2 shows typical TEM images of nanocomposites loaded with 1, 3 and 5 wt% organoclay. It is obvious from the TEM micrograph of the nanocomposite containing 1 wt% organoclay (Figure 2(a)) that the majority of individual clay sheets are dispersed homogeneously in the epoxy resin exhibiting the characteristic of a completely exfoliated clay nanosheets. Figure 2(b) shows that some of the organoclay platelets are intercalated and even exfoliated, along with some clay particles that were neither exfoliated nor intercalated in the sample with 3 wt% nanofiller. At the higher loading of nanofiller (5 wt%), some clusters of nanoclay exist consisting of various number of layers (marked by red circle in Figure 2(c)).

Accelerated Weathering Tests. Young's modulus and tensile strength for the neat epoxy matrix and corresponding

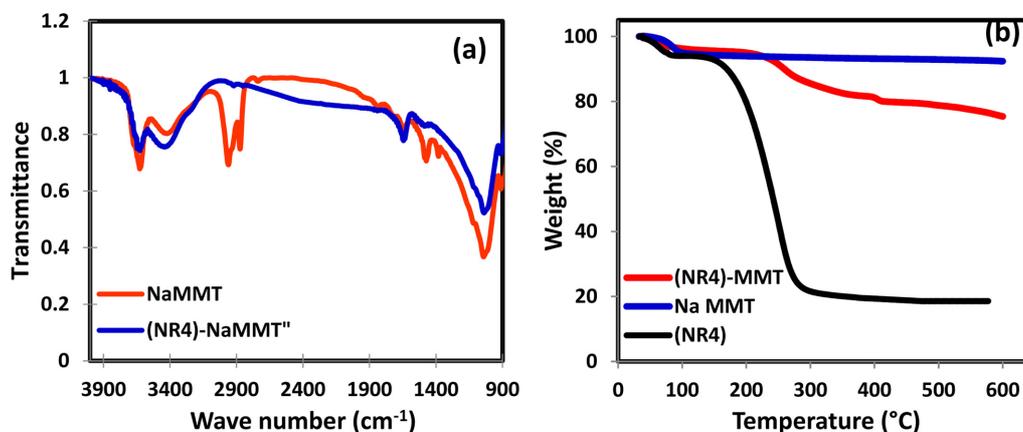


Figure 1. (a) FTIR spectra of primary nanoclay (NaMMT) and nanoclay modified with Tetra ((NR₄)-NaMMT); (b) TGA curves of primary nanoclays, modified nanoclay and neat Tetra (NR₄).

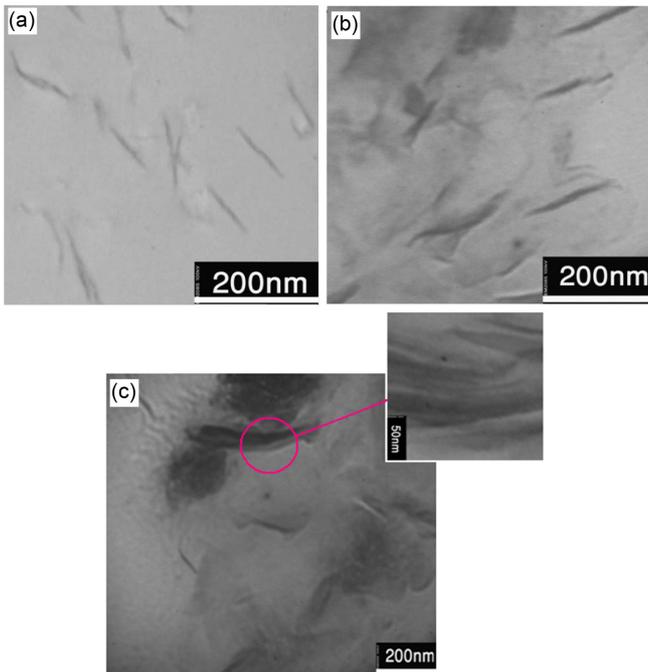


Figure 2. TEM patterns of the epoxy nanocomposites containing: (a) 1 wt%; (b) 3 wt%; (c) 5 wt% modified-nanoclay (organoclay).

nanocomposites are presented in Figure 3. As it can be seen in Figure 3(a), the modulus of all nanocomposites is higher than that of neat epoxy within the entire filler content range, and also modulus of nanocomposites increased with increasing organoclay content. Moreover, tensile strength was slightly enhanced up to 4 wt% nanoclay loading, then it was reduced at 5 wt% nanoclay (Figure 3(b)), mainly due to the deteriorated particle dispersion.²⁴

Furthermore, modulus and strength of the samples before

and after being subjected to the accelerated weathering by either temperature-humidity (WT) or by combined UV radiation and condensation (UWT) are compared in Figure 3(a) and (b), respectively. As it can be seen from Figure 3 and Table 1, modulus and tensile strength of all the samples were reduced after UV exposure, and the level of decline depended on the organoclay content. For the neat epoxy, the reduction in modulus and strength was most dominant and reached 11.3 and 32.0% after the UWT condition, respectively (Table 1). Whereas the embedding of organoclay into the epoxy matrix noticeably increased its mechanical durability against the UWT accelerated condition, which was revealed in the noticeable lower modulus and strength losses of nanocomposites as compared to the unfilled epoxy. The loading of 3 wt% organoclay led to maximum durability against UWT condition, as it demonstrated only 5.7 and 2.0% decrease in the modulus and strength, which are ≈ 2 and ≈ 16 times lower than the modulus and strength loss of the neat matrix after UV exposure.

After subjecting samples to the temperature-humidity condition (WT), modulus and tensile strength slightly reduced and the reduction amount is nearly same for the unfilled and nanoclay loaded samples. It is most likely that tensile modulus and strength were mostly determined by the bulk material which was not noticeably affected by WT condition. On the other hand, the relatively higher mechanical properties declined after UV exposure and also the dominant improvement in the mechanical properties retention in the presence of nanoclay can imply that the UWT weathering caused bulk degradation of specimens.

The samples started to lose weight by an epoxy erosion process, which was correlated to the synergistic physicochemical

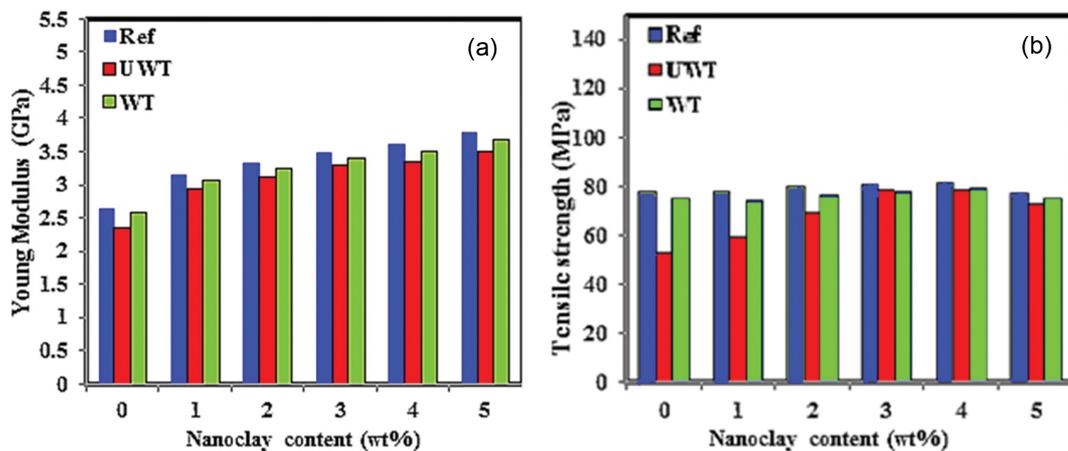
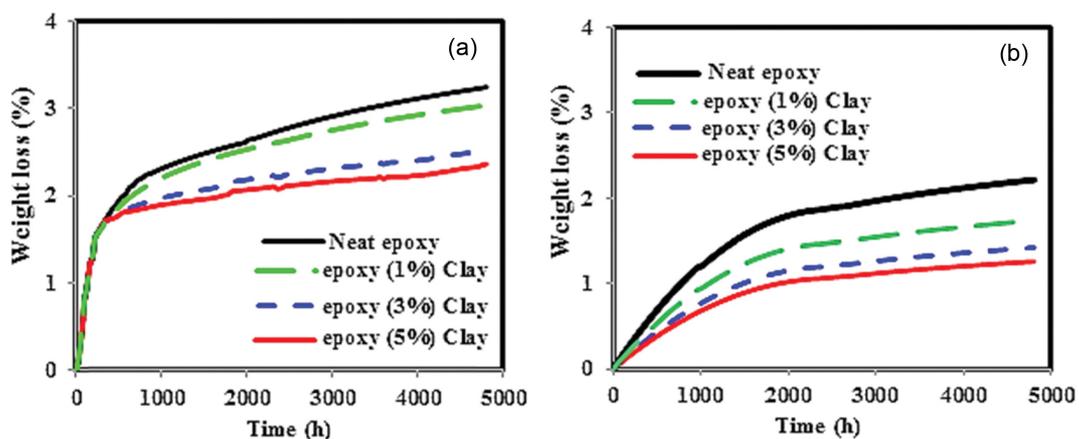


Figure 3. Effect of UWT and WT environments on (a) Young's modulus; (b) tensile strength of the epoxy/modified-nanoclay composites.

Table 1. Values of the Tensile Strength, Modulus and Weight Losses of Specimens after Subjecting to the UWT and WT Conditions

Organoclay content (wt%)	Strength loss (%)		Modulus loss (%)		Weight loss (%)	
	After UWT	After WT	After UWT	After WT	After UWT	After WT
0	32.0	3.7	11.3	1.8	3.2	2.2
1	23.3	4.2	6.6	2.0	3.0	1.7
2	14.0	2.4	6.9	1.9	-	-
3	2.0	3.3	5.7	2.1	2.5	1.4
4	6.7	3.0	7.2	2.5	-	-
5	9.0	3.5	7.9	1.7	2.3	1.2

**Figure 4.** Weight loss of neat epoxy and its corresponding nanocomposites during the accelerated environment of (a) UWT; (b) WT.

degradation of epoxy during exposure to the weathering conditions.²⁵ Hence, following the weight loss of samples as a function of the exposure time can be a representative of the degradation level of specimens. Figure 4(a) and (b) show the weight loss of the samples during the combined UV radiation and condensation condition (UWT) and temperature-humidity (WT) conditionings, respectively.

It can be clearly seen that the neat epoxy specimen exhibited greater weight loss, as compared to epoxy-clay nanocomposites at the end of the both conditions. Also, increasing the nanoclay concentration led to decrease weight losses, especially at the higher exposure times; as unfilled epoxy had weight loss of 3.2 and 2.2% while epoxy/clay nanocomposite loaded with 5 wt% displayed 2.3 and 1.2% weight loss after exposure to the UWT and WT weathering conditions, respectively (Table 1). These results are indicative of a greater degradation for the former material due to synergistic erosion of the epoxy matrix.²⁵ Therefore, it is worth noting that the presence of organoclay nanoparticles led to increased environ-

mental durability of epoxy resin in either humidity or UV radiation. The organoclay decreases both water uptake and diffusivity compared to the unfilled epoxy²⁶ with creating a longer diffusion path of water molecules into the nanocomposites,²⁷ and accordingly enhances durability of material during exposure to the weathering conditions.

Conclusions

In this study, the effect of accelerated weathering conditions on the durability of the epoxy resin reinforced with the surface modified nanoclays was investigated. Specimens were subjected to two environmental conditions: combined UV radiation and condensation and constant temperature-humidity. Generally, tensile strength and modulus of epoxy resin were enhanced with increasing organoclay nanoparticles concentration. In addition, tensile strength and modulus decreased after UV exposure, with much less extent for the nanocomposite than the neat epoxy. The embedding of organoclay

nanoparticles in epoxy resin led to enhancement of mechanical properties resistance to environmental degradation for combined UV radiation and condensation, but not for moisture. Moreover, the weight loss of the specimens was reduced noticeably at high organoclay contents in either temperature-humidity or combined UV radiation and condensation.

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