

Effect of Weathering on the Properties of Hybrid Composite Based on Polyethylene, Woodflour, and Nanoclay

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Hybrid composites of polyethylene/wood flour/nanoclay with different concentrations of nanoclay were fabricated using melt compounding followed by injection molding. Composites were weathered in a xenon-arc type accelerated weathering apparatus for 2000 h. Physical properties of the composites were evaluated by colorimetry and water absorption before and after weathering. Changes in surface chemistry were monitored using spectroscopic techniques. The results indicated that water absorption of the composites increased after weathering, but nanoclay can reduce the intensity of weathering to some extent by decreasing water absorption. Weathering increased the degree of color change and lightness of the samples; however, the lightness of the samples containing nanoclay was less than that of neat wood-plastic composites. Fourier transform infrared spectroscopy revealed a lower carbonyl index of composites containing nanoclay. X-ray diffraction patterns revealed that the nanocomposites formed were intercalated. The order of intercalation for samples containing 2 wt% nanoclay was higher than that of 4 wt% at the same maleic anhydride grafted polyethylene content, due to some agglomeration of the nanoclay.

Keywords: NanoWPC; Weathering; Water absorption; Colorimetry; Carbonyl index

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INTRODUCTION

The use of wood-plastic composites (WPCs) by the construction industry has resulted in concern about the durability of these products when exposed to outdoor environments. Of particular concern is the durability of WPCs after ultraviolet (UV) exposure (Stark and Matuana 2004). The weathering resistance of WPCs is generally poor, and discoloration, chalking, and dimensional changes caused by exposure are major problems with their use outdoors (Stark *et al.* 2003). The effect of accelerated UV weathering on color changes of polypropylene/aspen fiber composites was studied. The color changed from brown to chalky white (Rowell *et al.* 2000). The accelerated ultraviolet weathering of hot press-molded, recycled polypropylene sawdust composites with a combination of UV radiation and water spray was investigated. The results showed that water absorption and thickness swelling of the composites increased after accelerated weathering. The surface of the composites underwent significant color changes and lightening after weathering (Adhikary 2009).

Nanoscience and nanotechnology have opened up a new way of developing WPCs (Lu *et al.* 2006). In particular, nanotechnology offers ways to improve the mechanical and physical properties of WPCs by using nanosized fillers (Ashori and Nourbakhsh 2009). The larger the filler, the more imperfect is the structure. Thus, as the fillers become smaller, structural perfection can be approached (Fischer 2003). However, it seems that nanoparticles have an accelerating effect, acting as catalysts for the photo-oxidation of high-density polyethylene (HDPE). Researchers examined different series of HDPE nanocomposites containing 2.5 wt% multiwall carbon nanotubes, pristine and modified montmorillonite, and SiO₂ nanoparticles (Grigoriadou *et al.* 2011). From a Fourier transform infrared (FTIR) spectroscopy study, it was found that SiO₂ and organically-modified montmorillonite cause a serious effect on HDPE during UV degradation, and new chemical compounds containing carbonyl, vinyl, and hydroxyl groups were formed. This means that nanoparticles have an accelerating effect, acting as catalysts to HDPE photo-oxidation.

Although a considerable number of studies have been published on the different aspects of wood-plastic composites, there have been few publications about the weathering properties of these materials containing nanoparticles. The aim of this study was to investigate the effect of nanosilicate layers on the weathering properties of WPCs. The physical properties of WPCs with nanoparticles were determined after weathering and compared to those of unexposed samples. To interpret these properties, the morphology of the nanoparticles was evaluated.

EXPERIMENTAL

Materials

The polymer matrix high density polyethylene (HDPE) with trade name 52518 was supplied by Jam Petrochemical Co. (Iran), and had a density of 0.952 g/cm³ and melt flow index (MFI) (190°C/2.16 kg) of 18 g/10 min. The particle size of aspen wood flour was 80 mesh (180 μm). Maleic anhydride-grafted polyethylene (MAPE), provided by Solvay with a density of 0.965 g/cm³ (MFI 7 g/10 min, 1 wt% maleic anhydride) was used as a coupling agent. Cloisite 15A is a natural montmorillonite modified with dimethyl-dehydrogenated tallow-ammonium chloride salt, having a d-spacing of 31.5Å° and modifier concentration of 125 meq/100 g clay; it was obtained from Southern Clay Products.

Methods

Before sample preparation, wood flour was dried at 70 ± 5°C for 24 h. HDPE, wood flour, nanoclay, and MAPE were then weighed and bagged according to the formulations given in Table 1. Mixing was carried out in a Haake internal mixer (sys 90, USA) equipped with a cam blade at 150°C and 60 rpm. First, HDPE was fed into the mixing chamber. After melting, nanoclay and the coupling agent were added. After mixing for 5 min, the wood flour was fed into the system. The total mixing time was 10 min. The compounded materials were then ground to prepare the granules using a pilot scale grinder (WIESER, WGLS 200/200 model). The resulting granules were dried at 105°C for 24 h. Test specimens were prepared by an injection molding machine (Imen

Machine, Iran) at 190°C. The specimens were stored in controlled conditions (50% relative humidity and 23°C) for at least 40 h prior to testing.

Table 1. Composition of the Studied Formulations

Sample code	HDPE content (wt%)	Wood flour content (wt%)	Nanoclay content (wt%)	PE-g-MA content (wt%)
45W	52	45	0	3
45W2N	50	45	2	3
45W4N	48	45	4	3

Weathering

Composites were placed in a xenon-arc type light exposure apparatus (Atlas Xenotest Beta), operated according to ASTM D 2565. Samples were mounted on a drum that rotated around a filtered xenon-arc bulb at 1 rpm. Each 2 h weathering cycle consisted of 102 min of UV exposure and 18 min of simultaneous deionized water spray and UV exposure with a black panel temperature of $63 \pm 2^\circ\text{C}$. Irradiance was monitored ($41.5 \pm 2.5 \text{ W/m}^2$) and voltage to the bulb was changed periodically to maintain constant irradiance. Samples were removed for analysis after 2000 h of weathering.

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was conducted on a BRUKER Vertex-89 spectrometer to provide information about the functional groups present at the composite surface before and during the 2000 h of weathering. For each sample, 16 scans were recorded in absorbance units from 4000 to 600 cm^{-1} . Spectra were obtained using attenuated total reflectance (ATR). Using FTIR spectra, the carbonyl index was calculated with the following equation,

$$\text{Carbonyl Index} = \frac{I_{1715}}{I_{2916}} \times 100 \quad (1)$$

where I represents the peak intensity. The peak intensities were normalized using the peak at 2916 cm^{-1} , which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was chosen as a reference peak because it changed the least during weathering.

X-ray Diffraction

X-ray diffraction (XRD) analysis was carried out with a Philips Model X'Pert MPD (Holland) with $\text{CuK}\alpha$ radiation ($\lambda = 1.78 \text{ \AA}$, 40 kV, 30 mA) at room temperature. The scanning rate was $1^\circ/\text{min}$.

Colorimetry

Color measurements of weathered WPC specimen surfaces were recorded using a BYK-GARDNER 45/0 GLOSS UV-Vis spectrometer (400 to 700 nm) in accordance

with ASTM D 2244. Spectrometer's Spectra Wiz software transformed spectral data into CIELAB color coordinates (L^* , a^* , and b^*) based on a D65 light source. Six replicates per WPC sample were measured. Total change in color (ΔE_{ab}) was calculated using the following equation.

$$\Delta E_{ab} = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (2)$$

where ΔL , Δa , and Δb represent the differences between the initial and final values of L^* , a^* , and b^* , respectively. An increase in L means the sample is lightening. A positive Δa signifies a color shift toward red, and a negative Δa signifies a color shift toward green. A positive Δb signifies a shift toward yellow, and a negative Δb signifies a shift toward blue.

Water Absorption

Water absorption tests were carried out according to ASTM D-7031-04. Five specimens of each formulation were selected and dried in an oven for 24 h at 102 ± 3 °C. The weight of dried specimens was measured to a precision of 0.001 g. The specimens were then placed in distilled water and kept at room temperature. The weight of the specimens was measured after 30 days.

Statistics

To determine the effects of weathering on properties, Student's two-tailed t-tests were carried out at $\alpha = 0.05$ for each sample, testing the data for significant differences due to weathering.

RESULTS AND DISCUSSION

Dispersion Behavior of Clay

The XRD patterns of nanoclay and WPCs with different percentages of nanoclay loading are shown in Fig. 1. The interlayer spacing was calculated according to Bragg's law,

$$n\lambda = 2d \sin \theta \quad (3)$$

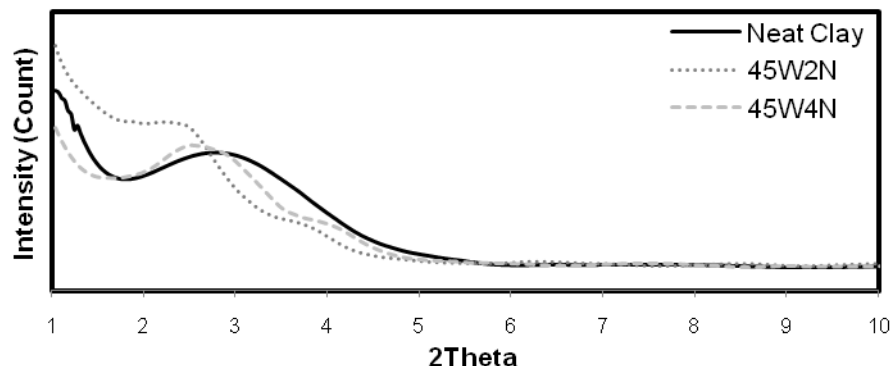


Fig. 1. XRD patterns of nanoclay content at 1° to 10°

It can be seen that the $2\theta = 2.80^\circ$ peak was related to neat clay with $d_{001} = 31.5 \text{ \AA}$. In the sample with 2% nanoclay, the peak shifted to a lower angle ($2\theta = 2.43^\circ$, $d_{001} = 36.32 \text{ \AA}$), which implies the formation of intercalation morphology. The peak related to 4% nanoclay appeared at $2\theta = 2.48^\circ$, $d_{001} = 35.53 \text{ \AA}$. These data show that the order of intercalation was higher at 2 wt% nanoclay than at 4 wt% nanoclay concentration. It seems that this is due to the limited value of coupling agents in the nanocomposites. In other words, MAPE in a lower concentration of clay has higher efficiency with respect to d-spacing of the layers.

Water Absorption

Figure 2 shows the water absorption of the samples *versus* nanoclay content. For all of the samples, it can be observed that the water absorption decreased as the nanoclay content increased. It can also be seen that the water absorption of all samples was higher after weathering. The comparison of water absorption of WPCs, before and after weathering, shows that it increased by 26.5%, while for nanoWPCs containing 2 wt% and 4 wt% nanoclay, the water absorption increased 24.7% and 22.6%, respectively. Therefore, it can be concluded that the water absorption of WPCs after weathering was higher than nanoWPCs. Generally, water absorption in WPCs is governed by two mechanisms: the hygroscopic nature of the fillers/fibers and the penetration of water into the composites (diffusivity) via gaps and flaws at the interfaces between fibers and plastics (Ghasemi and Kord 2009). Since composite microvoids and the lumens of fibers were filled with nanoclay, penetration of water into the deeper parts of composite was prevented (Ashori and Nourbakhsh 2011).

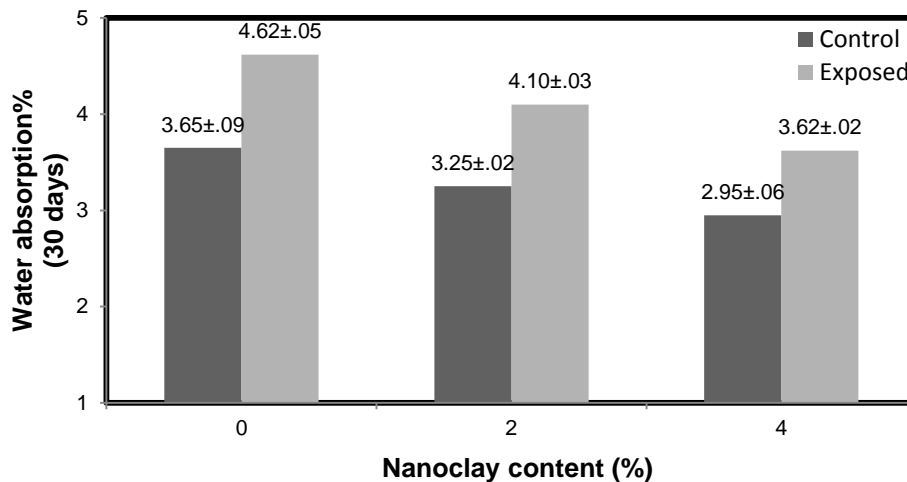


Fig. 2. Effect of nanoclay on water absorption (30 days) of exposed and control samples

On the one hand, weathering increases the wettability of the composites. Researchers have stated that the weathering increases the wettability of the wood component by reducing the water repellent effect of extractives, degrading the hydrophobic lignin component and exposing the cellulose-rich wood component at the composite surface layer (Colom *et al.* 2003). The increased hydroxyl groups from the exposed cellulose then promoted the water absorption and the thickness swelling of the composites.

On the other hand, it is well known that photo-degradation of HDPE can be accelerated by metal ions, which can be found in catalyst residues or in additives such as nanoparticles, resulting in increased water absorption of composites. It has been stated that organically modified montmorillonite has an accelerating effect, acting as a catalyst to HDPE photo-oxidation (Grigoriadou *et al.* 2011). It seems that both the clay and its ammonium modifier cause higher degradation in nanocomposites (Sánchez-Valdés *et al.* 2008). Therefore, it was expected that UV exposure of nanoWPCs would result in more severe weathering than WPCs and a subsequent further increase in water absorption. However, the results indicated that the water absorption of nanoWPCs (containing 4 wt% nanoclay) caused by weathering was less than that of the default WPCs. As mentioned above, nanoclay can fill composite microvoids and the lumens of fibers, so penetration of water into deeper parts of the composite is inhibited. It seems that the nanoclay plays a greater role in decreasing water absorption than in increasing weathering.

The structural changes of the WPCs and nanoWPCs were investigated via FTIR spectroscopy before and during the exposure to UV irradiation. The area that showed the most significant alterations corresponded to the carbonyl groups (1700 to 1800 cm^{-1}). It can be seen that WPCs and nanoWPCs displayed expanded peaks in this area, indicating the oxidation of the materials (Fig. 3a and b). The intensity of this peak increased continuously with increasing exposure time. Evidently, three major functional groups accumulated during degradation: ketones, carboxylic acids, and vinyl groups (Botta *et al.* 2009). The intensities of these peak areas also demonstrate the extent of photo-decomposition reactions. Comparing the carbonyl peak areas, it can be seen that this peak is stronger in WPCs than in nanoWPCs after the same exposure time, demonstrating that the presence of nanoclay in WPCs has a stabilizing effect.

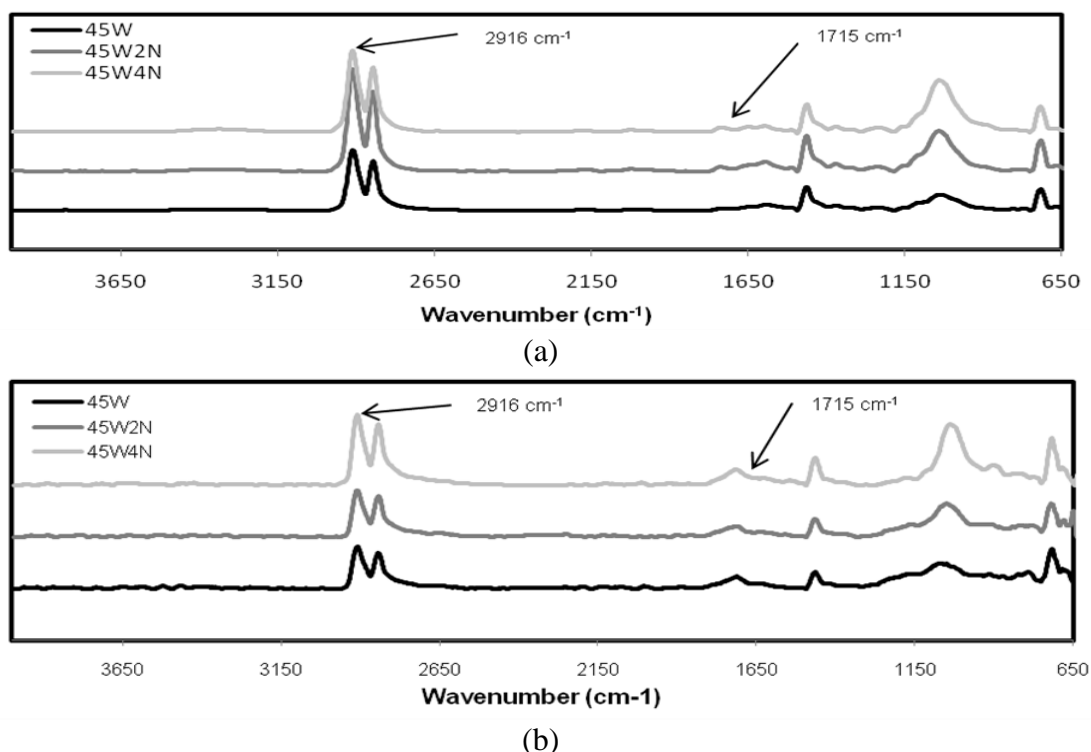


Fig. 3. FTIR spectra of (a) control and (b) exposed samples with (2 and 4 wt %) and without nanoclay

FTIR spectroscopy was used to determine structural changes in the HDPE and WPC surface chemistry after weathering. Carbonyl group formation indicates surface oxidation occurred (Hung et al. 2012; Lee and Cooper 2012). Figure 4 shows that the carbonyl index of all samples increased upon exposure time. Generally, the degradation reactions proceed from carbonyl group precursors (produce during polymer manufacture) according to Norrish type I and II reactions. If degradation of the carbonyl groups proceeds according to the Norrish I reaction, the resultant free radicals can attack the polyolefin, which may lead to termination via crosslinking or chain scission. If the degradation proceeds according to the Norrish II reaction, carbonyl groups and terminal vinyl groups are produced and chain scission occurs. In addition, the carbonyl group formed is capable of further degradation (Stark and Matuana 2004). Therefore, due to increment of carbonyl index, it can be concluded that degradation reactions of WPCs and nanoWPCs likely proceed according to Norrish II reactions. Also it can be seen that carbonyl index of nanoWPCs was less than that of WPCs during exposure time. Therefore, it can be concluded that the addition of nanoclay to the WPCs causes a decrease in the carbonyl index. Water accelerates oxidation reactions, and water absorption also decreased with increasing nanoclay content (Stark and Matuana 2007; Kord *et al.* 2011). Therefore, it can be concluded that the nanoclay content can decrease carbonyl index.

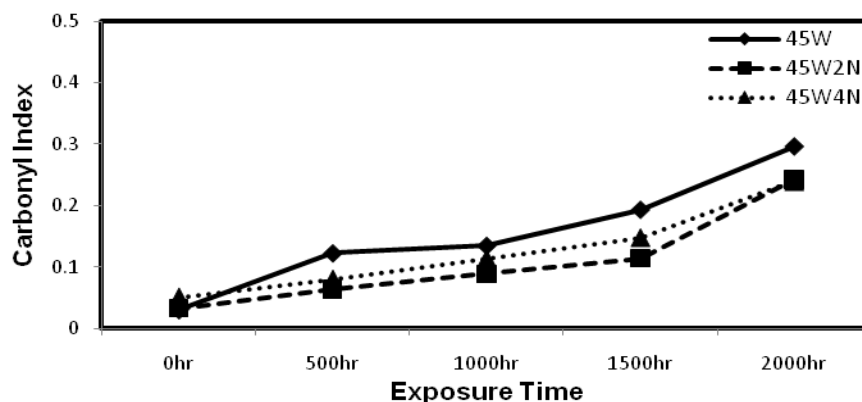


Fig. 4. Effect of nanoclay on the carbonyl index of samples

Colorimetry

Changes in color coordinates (Δa , Δb , and ΔL) and total color (ΔE) for the WPCs with different nanoclay contents after 2000 h of weathering were measured and are presented in Table 2. For reference the color coordinates of the reference samples (without and with nanoclay, prior to aging), were as follows: The values of L^* , a^* , and b^* for the samples without nanoclay were 28.83, -7.76, and 1.22, respectively. Also the values of L^* , a^* , and b^* for the samples containing 2 wt% nanoclay, were 28.81, -7.57, and 1.56, and those for the samples containing 4 wt% nanoclay were 28.11, -7.49, and 1.77 respectively.

As shown in the table, the color of samples (with and without nanoparticles) became much lighter after weathering. The ΔE values for WPCs and nanoWPCs also increased after weathering. However, WPCs containing 4 wt% nanoclay had the lowest values of ΔL and ΔE . The surface color of the WPCs turned white after weathering. NanoWPCs also showed discoloration after exposure, mainly resulting from increases in

lightness (Fig. 5). It should be noted that the relative increase of lightness for WPCs was 189%, while this value for the nanoWPCs containing 2 and 4 wt% nanoclay was 173.5% and 172%, respectively.

Table 2. Changes in Color Coordinates and Total Color of the Composites with Different Nanoclay Contents After 2000 h of Weathering

		ΔL	Δa	Δb	ΔE_{ab}
Sample code	45W	54.49	8.03	3.77	55.20
	45W2N	49.98	9.17	7.76	51.42
	45W4N	48.46	9.87	10.99	50.66

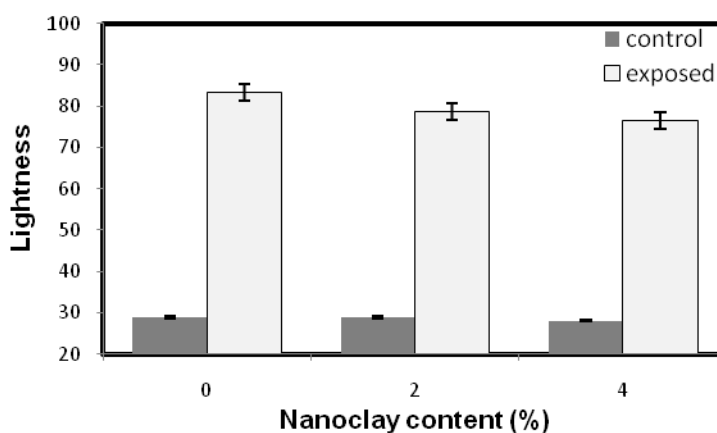


Fig. 5. Effect of nanoclay on the lightness of control and exposed samples

It has been stated that composites are subject to a lower degree of lightening when they are exposed to only UV light, compared with exposure to a combination of UV light and water spray (Stark 2005). Water accelerates oxidation reactions and causes the wood fiber to swell, creating more openings for light penetration. Additionally, water can remove some water-soluble extractives that impart color to the wood particle (Stark and Matuana 2007). Therefore, it can be supposed that the addition of nanoclay may contribute to less lightening because nanoclay decreases water absorption. Interestingly, the results confirmed this hypothesis because the samples with 4 wt% nanoclay content had the lowest change in lightness.

CONCLUSIONS

Hybrid composites are materials made by combining two or more different types of fibers in a common matrix. By hybridization, it is possible to achieve a balance between performance properties and cost of the composites, which would not be obtained with a single kind of reinforcement. This work addresses some key issues related to the weathering of hybrid composites based on HDPE/WF/nanoclay, which were prepared with different nanoclay concentrations. The accelerated weathering conditions (2000 h and xenon) were applied to the samples and the properties of the samples were determined after weathering. The following can be concluded:

The use of nanoclay can improve the performance of WPC relative to weathering.

1. The general trend of WPC weathering showed that surface oxidation increased after exposure. However, after 2000 h of weathering, the nanoWPCs showed a lower carbonyl index compared to WPCs.
2. The water absorption of the weathered samples increased, compared to those of the corresponding control samples, after 30 days of water exposure. The addition of nanoclay to the composites improved the water absorption. However, water absorption of weathered nanoWPCs was less than that of weathered WPCs.
3. Discoloration of WPCs caused by weathering was reduced by the addition of nanoclay. The addition of nanoclay can provide indirect protection against the deleterious effects of weathering, resulting in less lightening through decreasing water absorption and its oxidative role.
4. An intercalated morphology was observed for the hybrid nanocomposite. The order of intercalation for samples containing 2 wt% nanoclay was higher than that of 4 wt% at the same MAPE content, due to some agglomeration of nanoclay.

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