Environmental Degradation of Epoxy-Organoclay Nanocomposites Due to UV Exposure: Part I Photodegradation

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Abstract

The environmental degradation mechanisms of epoxy-organoclay nanocomposites due to accelerated UV and moisture exposure are studied. Various characterisation tools, including FTIR, SEM, XRD and XRF analyses, were used to evaluate the effects of clay content on the progressive changes in chemical element, topography and colour of the nanocomposite. It is found that microcracks started to appear on both the neat epoxy and nanocomposite surface after about 300 h of UV exposure. The nanocomposite exhibited thicker and shallower cracks with a less degree of discoloration than the neat epoxy due to the diffusion barrier characteristics of organoclay with high aspect ratio. The presence of transition metal ions along with low-molecular-weight organic modifiers in organoclay, however, accelerated the degradation of polymer, counterbalancing the above ameliorating barrier properties of clay. FTIR analysis indicated that photo-degradation generated carbonyl groups by chain scission and the rate was slightly higher for the nanocomposites than for the neat epoxy. While moisture further accelerated the photo-degradation process through the enhanced mobility of free radicals and ions, the organoclay could limit the deteriorating effect of moisture, resulting in much better overall resistance to photo-degradation in the presence of moisture for the nanocomposite than the neat epoxy.

Keywords: A. Nano-structures; A. Polymer-matrix composites (PMCs); B. Environmental degradation; D. Chemical analysis; A. Epoxy/Clay Nanocomposite

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1. Introduction

Polymer-organoclay nanocomposites are considered a new class of advanced organic-inorganic materials. The organoclay consists of layered silicate sheets, mineral oxides and other low-molecular-weight organic modifiers, and possesses unique capabilities valuable to the nanocomposites, which cannot be found in conventional micrometer-scale particulate reinforcements. Since the early work on montmorillonite reinforced nylon nanocomposite [1], organoclay nanocomposites have received significant attention in recent years due to their potential applications in many engineering components and structures. Nanocomposites based on thermoset or thermoplastic matrices exhibited much improved mechanical properties, thermal and chemical stability as well as barrier characteristics, compared to the neat polymers. Improvements in strength and modulus of nanocomposites were often gained at the expense of ductility. The elongations at break of nanocomposites were reduced with increasing clay contents [2-4].

The excellent barrier capability arising from the extremely high aspect ratio of clay is one of the most attractive properties of nanoclay composites, which has just started to be exploited in practical applications. The barrier characteristics are manifested by reduced permeability of moisture, gases and solvents, improved chemical resistance, reduced swelling in solvents as well as high flame retardant properties compared to neat polymers [5,6]. Associated with the permeability reduction are improved dimensional and thermal stabilities of nanocomposites. Dimensional stability against temperature fluctuations is an important characteristic for all coating and adhesive materials.

The decay of civil infrastructure in many developed countries has created a potential market for clay nanocomposites as protective coatings, adhesives and matrices for concrete structures and fibre-reinforced plastics for structural repair. These applications conventionally make use of thermosetting polymers, such as epoxy-based systems, and should possess high mechanical properties, good adhesion with cement/concrete, as well as high fire resistance and good weatherability against UV, alkaline and saline environments. They should also be resistant to

damage and property degradation against moisture absorption, cyclic loading and thermal fatigue often encountered in concrete structures. If these different weathering situations are acting concurrently, the material degradation process becomes even worse and more complex than the individual conditions acting alone. For example, rainfall or condensed water would wash away the photo-degraded chemicals caused by sunlight, exposing fresh surfaces for continued damages.

With specific applications as protective coatings in mind, the present paper is the continuation of our previous work on barrier characteristics of polymer-clay nanocomposites [5,6]. The degradation behaviour and residual properties of epoxy/clay nanocomposites were evaluated after accelerated UV exposure and extended moisture absorption.

2. Experiments

2.1 Materials and Sample Preparation

The epoxy resin used in this study was basically the same as the adhesive that has been employed for bonding of fibre reinforced plastics (FRPs) on reinforced concrete for strengthening and/or rehabilitation of concrete structures [7,8]. The resin consisted of a diglycidyl ether of bisphenol A (DGEBA) epoxy (MRL-A3), which was mixed with a MRL-B2 hardener (both supplied by Reno) in the ratio of 100: 35 by mass. The organoclay, Nanomer I.30P (supplied by Nanacor), is an octadecylamine modified montmorillonite suitable for dispersion into epoxy resin [5,9]. The required amount of organoclay was dried overnight at 75 °C in an oven prior to use. The epoxy was stirred using a high-speed shear mixer (supplied by Ross) to lower the viscosity before adding the clay. Mixing was then performed at a high shear rate of 3000 rpm for 1 h at room temperature. The mixture was subsequently sonicated for 3 h to further disperse the clay, and then degassed in a vacuum oven. The curing agent was added while the mixture was slowly stirred. To cast a nanocomposite plate, the resin mixture was poured into an aluminum mould consisting of a rectangular cavity surrounded by a Teflon dam 3 mm in thickness. The nanocomposite was then cured at room temperature for 7 days, followed by a postcure at 125 °C for 2 h to ensure complete

cure of resin. The translucent colour of the mixture and the cured nanocomposite plate with clay contents up to 5 wt% indicates uniform dispersion of organoclays, confirming the efficiency of the sonication processes used.

2.2 Characterization of Nanocomposites after UV Exposure

The degree of dispersion of the layered silicates and the corresponding interlayer distance within the epoxy matrix were studied using an X-ray diffraction analyzer (XRD, Philips PW1830). The XRD analyzer consisted of a Cu anode and a graphite monochromator, and the spectra were obtained at room temperature on a θ - θ diffractometer equipped with an intrinsic germanium detector system using Cu K α radiation (1.540562 Å) at a scanning rate of 0.01°/min from 2° to 10°. The clay particles were analysed using X-ray fluorescence spectroscopy (XRF, Jeol JSX-3201Z) to obtain information about elemental compositions. A transmission electron microscope (TEM, Jeol 2010) was used to evaluate the dispersion state of clay in the epoxy matrix. Ultra-thin samples obtained from the ultra-microtoming method were examined at an acceleration voltage of 120 kV.

3 mm thick samples made with neat epoxy, 3 wt% and 5 wt% clay nanocomposite were subjected to UV exposure in a chamber (Xenon Weather-Ometer, Atlas Ci4000) for different durations up to 2000 h, according to ASTM G26-C [10]. The environmental condition was set at 42 ± 3 °C and 30 ± 5 %RH, and the wavelength of radiation was 340 nm. Scanning electron microscopy (SEM, Jeol 6300) was used to examine the morphological changes of the nanocomposites after photo-degradation. The gradual changes in specimen colour during the UV exposure were evaluated using an image analyzer (Global Lab Image/2). Photographs were taken of the exposed specimens and the luminance values were calculated based on the weighted sum of RGB (Red, Green, Blue) system. The degree of brightness of the specimens was also given in the range between 0 (pure black) and 240 (pure white). Specimens approximately 200 μ m thick were prepared using a diamond saw to quantify the evolution of degraded chemical species on a Fourier transform infrared spectroscope (FTIR, Bio-Rad FTS 6000). The transmission mode was used in the wave-number range of 700~4000 cm^{-1} and at a resolution of 4 cm^{-1} . Specimens were examined

at an interval of 60 h for up to 360 h of UV exposure.

2.3 UV Exposure after Moisture Saturation

Both the neat epoxy and nanocomposite plates were cut into specimens of 200 μ m thick, which were stored in an environmental chamber at 25 °C and 98 %RH until they became fully saturated with moisture from monitoring the weight gains. Moisture saturated specimens were subsequently subjected to UV exposure for different durations using the same environmental conditions as the dry specimens, i.e. at 42 ± 3 °C and 30 ± 5 %RH. The photo-degraded specimens were analysed using a FTIR spectroscope in the same manner as the dry specimens to compare the degradation performance and thus to evaluate the influence of the presence of moisture on photo-degradation behaviour.

3. Results and Discussion

3.1 Dispersion of Organoclay in Nanocomposite

The XRD spectra shown in Fig. 1 indicate that the I.30P clay exhibited a peak of basal reflections of (001) plane with an intergallery distance or d-spacing of 2.24 nm. For the cured nanocomposites with varying clay contents, the (001) peak has completely disappeared suggesting that it has shifted to an angle below 2°, beyond the capacity of the XRD machine used in this study. This also means that the d-spacing increased to above 4.4 nm due to intercalation and/or exfoliation of the organoclay. The TEM photograph shown in Fig. 2 further confirmed the above observation. The dark lines represent individual layered silicates on a nanoscopic scale, suggesting that the interlayer distance increased to over 10 nm on average. Although the clay layers retained more or less the original stacking arrangement, they were heavily intercalated and some partially exfoliated. This observation testifies that the processing technique used in this study, including high speed shear mixing and ultrasonication, was effective in obtaining uniform dispersion of clay particles in the matrix. The high-speed shear mixer initially dispersed the clay particles in the epoxy on the microscopic scale, and subsequent nanoscopic dispersion was facilitated by the

ultrasonic energy which overcame the electrostatic attraction between the silicate layers. The insertion of epoxy and curing agent into the intergallery space of clay ensued, allowing further separation of intergallery distance during the chemical reaction upon curing.

3.2 Microcracking due to UV Exposure

Fig. 3 and 4 show, respectively, the surface morphologies of neat epoxy and epoxy/clay nanocomposite at different stages of UV exposure. Microcracks started to appear on the neat epoxy sample surface as early as about 300 h of UV exposure. The microcracks propagated deeper into the material and became broadened in width with further UV exposure. Similar microcracking phenomenon has been reported previously [11,12]: upon UV exposure, molecular chain scission occurred on the polymer surface to generate the polymer radicals. The fragments may link to the main chain of a neighboring molecule to give a branched molecule with a higher molecular weight. The excessive embrittlement resulting from the generation of these cross-linked molecules was mainly responsible for the formation of microcracks. The broadening of microcracks further exposed new material, accelerating the photo-degradation process.

Judging from the microscopic morphology shown in Figure 4, it can be said that the initial degradation behaviour of organoclay nanocomposites at the early stage of UV exposure was much similar to that of the neat epoxy. Microcracks started to appear after about 300 h of UV exposure, similar to the neat epoxy. However, crack propagation behaviours after a prolonged exposure for more than 1000 h were somehow different between the neat epoxy and nanocomposites. A closer examination of Figures 3(d)-3(f) and 4(d)-4(f) suggests that the cracks on the nanocomposite surface were wider and shallower than those on the neat epoxy, as a result of the presence of organoclay in the nanocomposites. (Note that the magnifications in both figures are the same.) This observation may be attributed to several reasons. The excellent barrier characteristics of clay can delay the penetration of oxygen and free radicals into the polymer, which are typical species essential to the process of photo-degradation. Once these species are effectively prevented from deep penetration, they tend to accumulate on the top surface and cause more damage to the surface

layer. This results in a shallower crack profile for the nanocomposite than in the neat epoxy. Another important factor that affected the surface damage process in the nanocomposite is the organic modifier applied to the clay (occupying as much as 25-30 wt% of the whole clay). The octadecylamine modifier used for the I.30P clay is a polymer with a low molecular weight, which is extremely susceptible to degradation [13] under UV exposure. Moreover, the unexchangeable cations that may be present at the intergallery space, particularly transition metals like Fe^{2+} and Fe^{3+} , can further accelerate the decomposition of hydroperoxide and hence the photo-degradation rate by the reaction process schematically shown in Fig. 5 [14-16]. The presence of these transition metal ions was confirmed by the XRF analysis as indicated in Table 1.

3.3 Discolouration due to UV Exposure

The photo-degradation process can be manifested by discolouration through darkening or yellowing of polymer. The darkening effect was evaluated with the aid of an image analyzer to calculate the luminance values. After selecting the region of interest (ROI), the luminance values in terms of individual pixels in ROI were collected and plotted as a histogram. The luminance values, L , given in Fig. 6 are the average of all pixels (around 5000 in total) in the selected ROI of 5 mm x 5 mm square. It should be noted that the thickness of all specimens was kept constant at 3 mm, by using a Teflon shim of the same thickness during mould casting. The incorporation of organoclay turned the nanocomposites darker as reflected by the lower L values than the neat epoxy before UV exposure. This finding is consistent with previous reports [17,18]. Upon UV exposure, all specimens became darker as a direct reflection of the alteration of chemical elements constituting the photo-degraded polymer. As a summary of the results in Fig. 6, Fig. 7 shows the general trend of luminance against UV exposure time. The L values for all specimens dropped gradually at the beginning of exposure and reached a plateau after about 700 h of exposure. The numbers given in the inset of Fig. 7 represent the difference in luminance between 0 h and 2000 h, i.e. $L_0 - L_{2000}$, which suggests reduced discoloration rate in absolute terms with increasing clay content. This conclusion holds despite the fact that the normalized luminance (L/L_0) exhibited essentially similar

behaviours between the neat epoxy and nanocomposites. The beneficial effect of organoclay in nanocomposites arises from the barrier characteristics of silicate layered structure, which also signifies the importance of uniform dispersion and exfoliation of clay within the matrix in promoting the barrier characteristics.

3.4 Changes in Elemental Composition due to UV Exposure

The FTIR analysis was performed to monitor the change in chemical species and degraded products, from which the degradation rates were determined. Previous studies [15,16,19-21] suggested that photo-degradation generates carbonyl and hydroxyl groups through chain scission and hydrogen abstraction from the polymer backbone. The degradation process is summarised in Fig. 8 according to Rabek [16]. Fig. 9 presents the evolution of the peaks corresponding to the olefinic and carbonyl groups over the prolonged UV exposure, which were obtained from the FTIR analysis. Both the neat epoxy and epoxy/clay nanocomposites exhibited essentially similar behaviour with respect to UV exposure time. Two prominent peaks were revealed at wavenumbers of 1659 cm^{-1} and 1724 cm^{-1} , which represent the stretching vibrations of olefinic ($\text{C}=\text{C}$) and carbonyl ($\text{C}=\text{O}$) groups, respectively. The generation of these double bonds commonly arises from bond dissociation by photo-degradation. The $\text{C}=\text{C}$ and $\text{C}=\text{O}$ groups belong to the chromophoric groups, which tend to absorb the light by exciting an electron from their ground state into excited state when exposed to UV radiation. Once these chemical species absorb certain visible wavelengths and transmit or reflect others, discolouration occurs in the polymer [22].

A further analysis was made by evaluating the net changes in chemical elements with respect to UV exposure duration. Fig. 10 presents net IR spectra for the specimens after UV exposure, which were obtained after subtracting the spectra corresponding to the unexposed specimens. The areas under the carbonyl bands in Fig. 10 were integrated to quantitatively measure the intensities of the carbonyl group, which are plotted as a function of exposure time in Fig. 11. The generation of olefinic species came from the recombination of alkyl radicals and this process happened throughout the degradation process provided that the alkyl radicals were present. However, since

the essential propagation step is the formation of hydroperoxides and its subsequent decomposition yielding alkoxy radicals (Fig. 8), the carbonyl species were generated as a result of β -scission from the alkoxy radicals. Thus, the intensity measured from the area under the carbonyl group has been used to indicate the relative degree of photo-degradation for different materials while the environmental conditions are set identical [15,19]. The intensities for both the neat epoxy and nanocomposite increased consistently with exposure time. The overall degradation with respect to exposure time was very similar between the two materials, with the neat epoxy marginally outperforming the nanocomposite. It can be concluded that the low molecular weight organic modifier and unexchanged transition metal ions present in organoclay both favoured accelerated degradation whereas the excellent barrier characteristics of clay [5,6] may have counterbalanced these effects, resulting in similar photo-degradation performance between the neat epoxy and the epoxy/clay nanocomposite.

3.5 Combined Effects of Moisture and UV Exposure

The combined effects of moisture absorption by the polymer and subsequent UV exposure were studied for the photo-degradation behaviour of the nanocomposites. The FTIR spectra were obtained for both the neat epoxy and the nanocomposite, from which the net IR spectra were similarly determined after UV exposure by subtracting those corresponding to the unexposed specimens. The results are presented in Fig. 12, showing that the intensities of the peaks corresponding to olefinic (C=C) and carbonyl (C=O) groups for the wet specimens were generally higher than those of the dry specimens (Fig. 10). Thus, the areas measured under the carbonyl bands are compared between the dry and wet specimens in Fig. 13. It is found that moisture further aggravated the photo-degradation performance of polymer regardless of the presence of nanoclay reinforcement or not. The overall intensities of photo-degradation for the two different materials with and without moisture saturation followed very much a similar trend with respect to exposure duration. However, the quantitative effects of moisture on intensity of photo-degradation were largely different between the neat epoxy and nanocomposite. The difference in intensity between

the dry and wet specimens measured at 360 h of UV exposure was much larger for the neat epoxy than for the nanocomposite (8.32 vs 1.43, as indicated by the arrows in Fig. 13). There are two major mechanisms that are responsible for the aggravated photo-degradation of polymer in the presence of absorbed moisture: (i) the water molecules enhance the photo-oxidative reactions due to the increased OH^- and H^+ ions [22]; and (ii) the water molecules can be located on the free volume sites between polymer molecules, improving the mobility of free radicals within the surface layer, thus accelerating photo-oxidation [23].

Obviously, the photo-degradation performance of the nanocomposite was much better than the neat epoxy in the presence of moisture. If the specimens were maintained fully saturated with moisture during the UV exposure, much more aggravated results would have been obtained. It is likely that the presence of clay may also delay the moisture diffusing out of the specimens during UV exposure. This would further reduce the harmful effect of moisture on degradation intensities. This ameliorating effect of clay nanoplatelets is consistent with the significantly reduced diffusivity and permeability of moisture and gas through the clay nanocomposites compared to neat polymer resins, which was proven in our previous studies [5,6]. Tortuous path models [24,25] have been developed to account for the enhanced barrier characteristics, where the clay platelets obstruct the passage of permeant through the bulk polymer.

4. Conclusions

The photo-degradation performance of neat epoxy and epoxy/clay nanocomposites due to accelerated UV exposure and moisture saturation was evaluated. The following can be highlighted from this study.

- 1) UV exposure resulted in photo-degradation of polymer surface with many microcracks that started to appear after about 300 h of exposure. The cracks on the nanocomposite surface were wider and shallower than those on the neat epoxy. While the excellent barrier characteristics of nanoclay delayed the penetration of oxygen and free radicals into the nanocomposite, the organic modifier and unexchangeable metal ions present in the

organoclay aggravated the degradation performance of nanocomposite.

- 2) UV exposure darkened the colour of the neat epoxy and nanocomposites. The luminance values for all specimens dropped gradually upon initial UV exposure and reached a plateau after about 700 h. The difference in luminance between different materials suggests increasingly less discolouration with increasing clay content, reflecting the excellent barrier characteristics of nanoclay.
- 3) The degradation intensities as measured by the areas under the carbonyl bands of FTIR spectra were similar between the neat epoxy and nanocomposites in the dry condition. Moisture further accelerated the photo-degradation process of polymer due to the increased OH^- and H^+ ions and improved mobility of free radicals in the presence of moisture. However, the deteriorating effect of moisture was significantly reduced by the excellent barrier characteristics of clay nanoplatelets that effectively restricted the movement of moisture and its interactions with radicals and oxygen, as suggested by the tortuous path models.

Acknowledgements

This project was supported by the Research Grant Council of Hong Kong Special Administration Region (Project Number HKUST6184/03E). Technical assistance from the Advanced Engineering Materials Facility (AEMF) and the Materials Characterization and Preparation Facilities (MCPF), HKUST is much appreciated. Part of the paper was presented at SAMPE '06 at Long Beach, CA, USA in May 2006.

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Table 1. Elemental compositions of I.30P nanoclay by XRF.

Elements	Si	Al	Mg	Na	Ca	Fe	O
Mass %	39.03	13.46	2.59	0.18	0.23	2.19	41.83

Figure Captions

- Figure 1** XRD spectra of (a) pure organoclay and cured epoxy/clay nanocomposites containing (b) 1 wt%, (c) 3 wt% and (d) 5 wt% of clay.
- Figure 2** TEM morphology of epoxy nanocomposites containing 3 wt% nanoclay.
- Figure 3** SEM microphotographs of degraded surfaces of neat epoxy after UV exposure of (a) 0 h; (b) 333 h; (c) 533 h; (d) 933 h; (e) 1500 h and (f) 2000 h.
- Figure 4** SEM microphotographs of degraded surfaces of epoxy/clay nanocomposite with 5 wt% clay after UV exposure of (a) 0 h; (b) 333 h; (c) 533 h; (d) 933 h; (e) 1500 h and (f) 2000 h.
- Figure 5** Schematic of accelerated hydroperoxide decomposition due to transition metal ions.
- Figure 6** Discolouration of (a) neat epoxy, (b) and (c) nanocomposites with 3 wt% and 5 wt% of I30P clay, respectively.
- Figure 7** Luminance values plotted as a function of UV exposure time for neat epoxy and epoxy/clay nanocomposites.
- Figure 8** Schematic of degradation process due to UV exposure (P: Polymer).
- Figure 9** Gradual development of olefinic and carbonyl groups in (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after UV exposure.
- Figure 10** Net FTIR spectra for (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after UV exposure for different durations. The net spectra were obtained after subtracting those corresponding to the unexposed specimens in Figure 8.
- Figure 11** Comparison of areas under the carbonyl bands for neat epoxy and epoxy/5 wt% clay nanocomposite as a function of UV exposure durations.
- Figure 12** Net FTIR spectra for (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after moisture saturation followed by UV exposure for different durations.
- Figure 13** Comparison of areas under the carbonyl bands for dry and wet specimens of neat epoxy and epoxy/5 wt% clay nanocomposite as a function of UV exposure durations. (Arrows represent the differences in area between the dry and wet specimens at 360 h of UV exposure.)

Figure 1 XRD spectra of (a) pure organoclay and cured epoxy/clay nanocomposites containing (b) 1 wt%, (c) 3 wt% and (d) 5 wt% of clay.

Figure 2 TEM morphology of epoxy nanocomposites containing 3 wt% nanoclay.

Figure 3 SEM microphotographs of degraded surfaces of neat epoxy after UV exposure of (a) 0 h; (b) 333 h; (c) 533 h; (d) 933 h; (e) 1500 h and (f) 2000 h.

Figure 4 SEM microphotographs of degraded surfaces of epoxy/clay nanocomposite with 5 wt% clay after UV exposure of (a) 0 h; (b) 333 h; (c) 533 h; (d) 933 h; (e) 1500 h and (f) 2000 h.

Figure 5 Schematic of accelerated hydroperoxide decomposition due to transition metal ions.

Exposure time, t (h)	Luminance, L	Photograph	Exposure time, t (h)	Luminance, L	Photograph
0	181.6		0	161.0
133	166.1		133	147.3
333	153.7		333	138.5
533	142.1		533	130.7
733	133.6		733	122.6
933	128.6		933	122.0
1500	123.0		1500	113.3
2000	120.7		2000	109.6

(a) (b)

Exposure time, t (h)	Luminance, L	Photograph
0	142.8
133	123.4
333	118.5
533	106.0
733	101.5
933	101.4
1500	98.5
2000	93.2

(c)

Figure 6 Discolouration of (a) neat epoxy, (b) and (c) nanocomposites with 3 wt% and 5 wt% of I30P clay, respectively.

Figure 7 Luminance values plotted as a function of UV exposure time for neat epoxy and epoxy/clay nanocomposites.

Figure 8 Schematic of degradation process due to UV exposure (P: Polymer). After Rabek [16].

(a)

(b)

Figure 9 Gradual development of olefinic and carbonyl groups in (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after UV exposure.

(a)

(b)

Figure 10 Net FTIR spectra for (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after UV exposure for different durations. The net spectra were obtained after subtracting those corresponding to the unexposed specimens in Figure 8.

Figure 11 Comparison of areas under the carbonyl bands for neat epoxy and epoxy/5 wt% clay nanocomposite as a function of UV exposure duration.

(a)

(b)

Figure 12 Net FTIR spectra for (a) neat epoxy and (b) epoxy/5 wt% clay nanocomposite after moisture saturation followed by UV exposure for different durations.

Figure 13 Comparison of areas under the carbonyl bands for dry and wet specimens of neat epoxy and epoxy/5wt% clay nanocomposite as a function of UV exposure durations. (Arrows represent the differences in area between the dry and wet specimens at 360 h of UV exposure.)