# Ultraviolet Light Aging Properties of PVC/CaCO$_3$ Composites

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**ABSTRACT:** The ultraviolet radiation aging behaviors of PVC/CaCO$_3$ and PVC/CaCO$_3$/macromolecular modifier composites were studied through whiteness measurement, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, scanning electron microscopy, and mechanical properties test. It was found that nano-CaCO$_3$ particles used as ultraviolet light screening agents could significantly enhance the antiaging properties of PVC materials. Due to the macromolecular modifier coated on nano-CaCO$_3$ particles, the compatibility of nano-CaCO$_3$ and PVC matrix was improved, resulting in uniform dispersion of nano-CaCO$_3$ in PVC matrix. Therefore, the PVC/CaCO$_3$/MP composite exhibited better antiaging properties than PVC/CaCO$_3$ composite. After 12 h of ultraviolet irradiation, the tensile strength retention, elongation at break retention, and impact strength retention of PVC/CaCO$_3$/MP composite were 79.5%, 74.5%, and 75.3%, which were much higher than that of neat PVC and PVC/CaCO$_3$ composite. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

## INTRODUCTION

PVC has been widely used in the construction, transportation, and many other industries due to its high stiffness, flame retardancy, and chemical resistance, as well as its low cost. However, the bad photostability of PVC has restricted its application. PVC materials undergo rapid autocatalytic dehydrochlorination upon exposure to sunlight during outdoor applications, following the formation of conjugated polyene sequences and the discoloration of materials.[1,2] All these chemical changes lead to the deterioration of the mechanical properties of PVC.

Many additives, such as ultraviolet light screening agents, ultraviolet absorber, excited-state quencher, and radical scavenger, are used to improve the PVC materials antiaging properties.[3–10] Inorganic fillers functioned as light shield agents could enhance antiaging properties of PVC.[11–16] A lot of researches about these topics have been reported. Day[17] mentioned that the strong absorption of most harmful wavelengths in solar radiation of TiO$_2$ resulted in the protection of the polymer matrix from photochemical degradation. Gesenhues[18] found that TiO$_2$ was not photo-catalytically active in dry irradiation of PVC, while the photo-oxidation of TiO$_2$-pigmented PVC became much faster during weathering at the same intensity. Zhang et al.[19] found that CaCO$_3$, talc and SiO$_2$ could hold up the UV aging

behaviors of PVC, while montmorillonite (MMT) and pyrophyllite fillers could accelerate the UV aging behaviors of PVC.

Inorganic particles used as fillers can not only enhance antiaging properties of PVC but also improve the mechanical properties of PVC and decrease its cost. However, the precondition is that inorganic particles could be well dispersed in PVC matrix. Due to the different interfacial properties of inorganic fillers and PVC matrix, it is quite difficult to make inorganic fillers uniformly disperse in PVC matrix. The aggregative inorganic fillers not only lead to the deterioration of the mechanical properties of PVC but also affect the antiaging properties of PVC composites. Therefore, many studies focused on the modification of inorganic fillers for PVC application.[20–25] Xie et al.[23] researched the rheological and mechanical properties of PVC/CaCO$_3$ nanocomposites prepared by *in situ* polymerization. The results showed that the glass transition and thermal decomposition temperatures of PVC phase in PVC/CaCO$_3$ nanocomposites were shifted toward higher temperatures by the restriction of CaCO$_3$ nanoparticles on the segmental and long-range chain mobility of the PVC phase. Xiong et al.[25] studied the mechanical and thermal properties of PVC/core-shell nano-CaCO$_3$ composites with ACR as shell and PMMA as surface modified agent. The resultant composites exhibited better mechanical properties
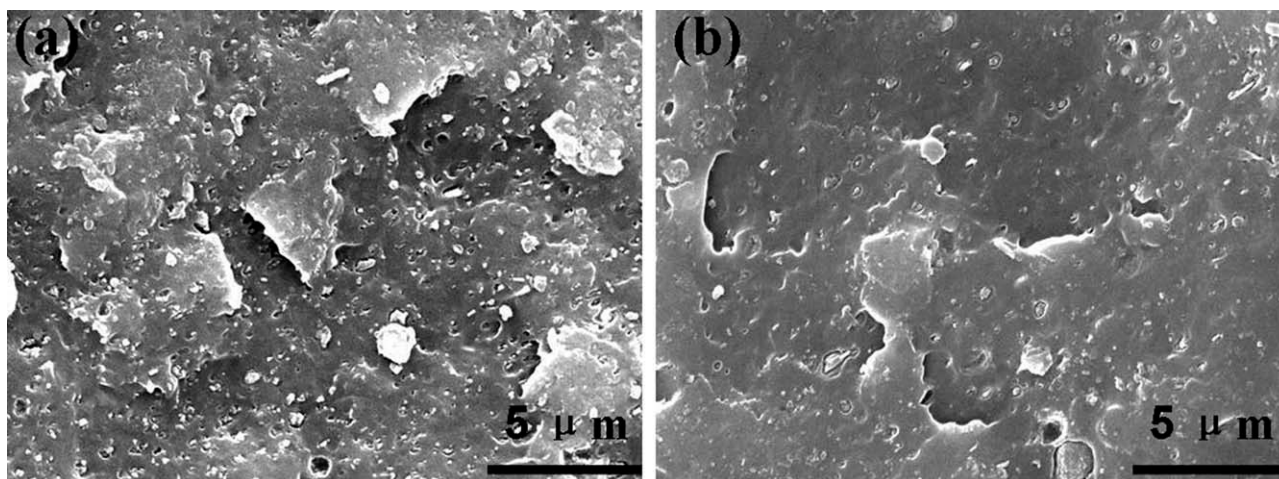
**Figure 1.** Fracture SEM micrographs of (a) PVC/CaCO₃ composite and (b) PVC/CaCO₃/MP composite at 8 phr nano-CaCO₃ particles.

and higher $T_g$ than neat PVC. Most of the researches were prone to study the mechanical and thermal properties of the PVC/modified inorganic fillers composites, while the reports about the antiaging properties of the PVC/modified inorganic fillers did not attract enough attentions.

Nano-CaCO₃ and macromolecular modifier coated nano-CaCO₃ were chosen to investigate the effects of modified inorganic fillers on antiaging properties of PVC matrix. The antiaging properties of the PVC/CaCO₃ and PVC/CaCO₃/MP composites were discussed, including whiteness retention, carbonyl index, double bond index, UV–vis absorbance, surface appearance, and mechanical properties.

## EXPERIMENTAL

### Materials
The PVC resin (SG5, $K = 66$) was purchased from Guizhou Jinhong Chemical Company. The processing aid acrylic ester (ACR-201) was supplied by Laiwu Chemical Company, Shandong, China. The other additives, such as a lead complex thermal stabilizer, calcium stearate, and external wax, were provided by Haolong Chemical Company, Tianjin, China. The nanoscale particle calcium carbonate was supplied by Nanomaterials Technology (Shanxi) with particle diameters ranging from 15 to 40 nm, and was used without further treatment. The macromolecular modifier (MP) was purchased from Shanghai Succeed Rubber. It was fairly compatible with PVC and widely used for the modification of PVC.

### Samples Preparation
First, the nano-CaCO₃ particles and MP were mixed in a high-intensity mixer for 120 s. The weight ratio of the nano-CaCO₃ particles and MP was 90/10. Second, varying percentage of mixed MP-coated nano-CaCO₃ particles, PVC, and other additives were dry-blended in a high-intensity mixer for 120 s. Then the mixing process was run at a constant mixer temperature of 175°C for 5 min. The rotor speed was 50 rpm and the weight charge was set at 75 g. Compared with the PVC/CaCO₃/MP composite, the PVC/CaCO₃ composite were prepared in the mixer at the same condition. All PVC samples were compressed into 4

and 2 mm thick sheets at 180°C and 20 MPa for 5 min. The 4 mm thick samples were machined into impact specimens (GB/T 1043-2002, $80 \times 10 \times 4$ mm³); the 2 mm thick samples were machined into tensile testing specimens (GB/T 1040-2002, $75 \times 10 \times 2$ mm³). The surface layer from the irradiated samples was used to the whiteness, FTIR, UV–vis, and SEM measurements.

### Accelerated Ultraviolet-Weathering Tests
Accelerated artificial ultraviolet weathering tests were conducted in a self-prepared chamber equipped with 500 W high pressure mercury lamp, ventilation, and heating equipment. The samples were subjected to continuous exposures at 40°C, and the average irradiation intensity was 5.5 W/m² at 340 nm. The accelerated irradiation test was completed after 4, 8, 12, and 16 h, respectively.

### Measurements and Characterization
The whiteness of samples before and after aging were recorded by using whiteness testing machine (Qingtong Machine, Hangzhou) according to GB2913-82 standard at room temperature. The whiteness retention was calculated as follow:

$$\mathrm{WR}_t = W_t / W_0$$

where, $\mathrm{WR}_t$ is the sample whiteness retention after aging $t$ hours, $W_t$ is the sample whiteness after aging $t$ hours, $W_0$ is the sample whiteness before aging.

The FTIR spectra were recorded by using a Thermo Nicolet Nexus spectrometer (Thermo Nicolet, America) between 4000 cm⁻¹ and 400 cm⁻¹ with a resolution of 2 cm⁻¹ at room temperature. The 1456 cm⁻¹ peak, which was attributed to the bending vibration of C—H, was selected as an internal reference. The carbonyl index (CI) was defined to show the photo oxidation degree of the material and the formation of the conjugated was characterized by the double bond index (DBI):

$$\mathrm{CI} = A_{\mathrm{C=O}} / A_{1456}$$
$$\mathrm{DBI} = A_{\mathrm{C=C}} / A_{1456}$$

where, $A_{\mathrm{C=O}}$ is the peak area of carbonyl group, $A_{\mathrm{C=C}}$ is the peak area of vinyl group, and $A_{1456}$ is the peak area of C—H.
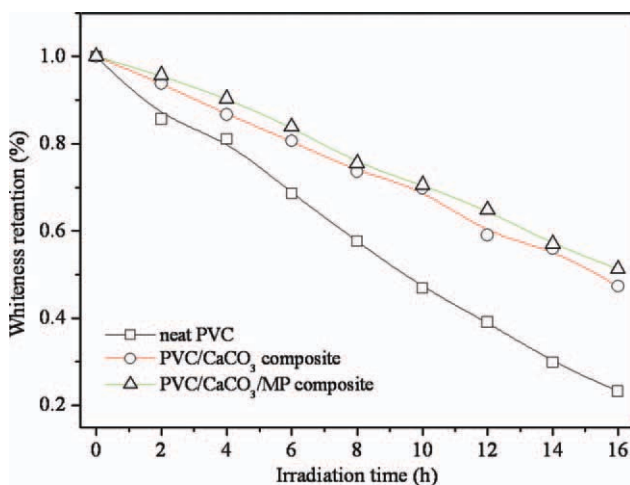
**Figure 2.** Whiteness retention of neat PVC and two kinds of composites in different irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The ultraviolet spectra of samples were collected by a Shimadzu 2550 ultraviolet–visible spectrophotometer in the wavelength range from 220 to 420 nm. The absorbance increment of the sample at selected wavelength was recorded as $\Delta A$, which calculated as follow:

$$\Delta A = A_t - A_0$$

where $A_t$ is the sample ultraviolet absorbance after aging $t$ hours, $A_0$ is the sample ultraviolet absorbance before aging.

The morphology of PVC sample's fractured surface obtained in notched impact and the surface morphological images of different PVC sheets after irradiation were taken by JSM-5610LU scanning electron microscope (Hitachi, Japan). All of the fractured surfaces were coated with gold-palladium film.

Tensile yield strength tests were performed according to GB1040-2002 standard. The tensile tests were conducted at a crosshead speed of 10 mm/min. Impact strength tests were performed according to GB1043-2002 standard at room temperature.

## RESULTS AND DISCUSSION

### Fracture Morphology Analysis

It is known that uniform dispersion and good compatibility are the main mechanism to explain the increased performances of PVC composites.[26] The dispersion and compatibility of nano-$CaCO_3$ particles are significantly improved when the nano-$CaCO_3$ particles are modified by MP. To evaluate the surface modification of nano-$CaCO_3$ particles, the SEM micrographs of PVC/$CaCO_3$ and PVC/$CaCO_3$/MP composites with 8 phr nano-$CaCO_3$ particles are shown in Figure 1.

Figure 1 shows SEM micrographs of the fracture surfaces of PVC/$CaCO_3$ and PVC/$CaCO_3$/MP composite respectively. From Figure 1(b), it can be seen that most of the $CaCO_3$/MP particles uniformly disperse in the PVC matrix, while a few particles agglomeration is observed. The dispersion of nano-$CaCO_3$ particles in PVC/$CaCO_3$ composite [Figure 1(a)] is worse than the

dispersion of $CaCO_3$/MP in PVC/$CaCO_3$/MP composite. There are many particles agglomeration observed in the fracture surface of PVC/$CaCO_3$ composite. Furthermore, the compatibility of $CaCO_3$/MP and PVC matrix is much better than the compatibility of nano-$CaCO_3$ particles and PVC matrix.

### Whiteness Analysis

The whiteness retention of neat PVC, PVC/$CaCO_3$, and PVC/$CaCO_3$/MP composites at varying aging times are shown in Figure 2. It is obviously that the whiteness retention of PVC/$CaCO_3$ and PVC/$CaCO_3$/MP composites are much higher than that of neat PVC. Also, it is interesting to note that PVC/$CaCO_3$/MP composite has a little higher whiteness retention than that of PVC/$CaCO_3$ composite. It means that nano-$CaCO_3$ particles and macromolecular modifier coated on nano-$CaCO_3$ particles enhance the antiaging properties of PVC resins, and the macromolecular modifier coated on nano-$CaCO_3$ particles have better effect than nano-$CaCO_3$ particles.

It is not completely clear that what accounts for the interesting phenomena described above. It is generally recognized that inorganic fillers, such as $TiO_2$, $ZnO$, and $CaCO_3$ particles, can use
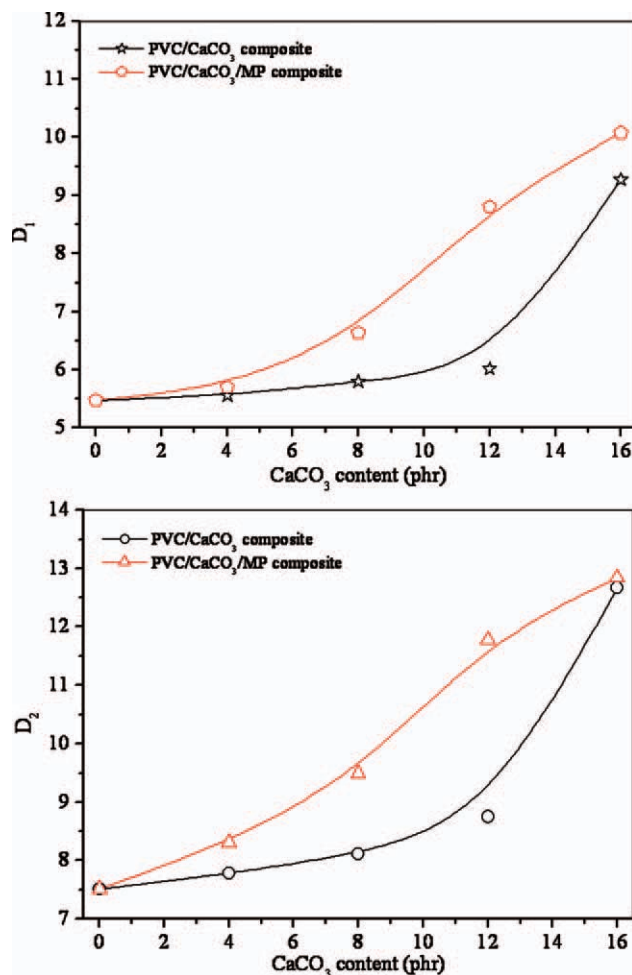


**Figure 3.** Antiaging time $D_1$ and $D_2$ of PVC composites at varying $CaCO_3$ particles contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
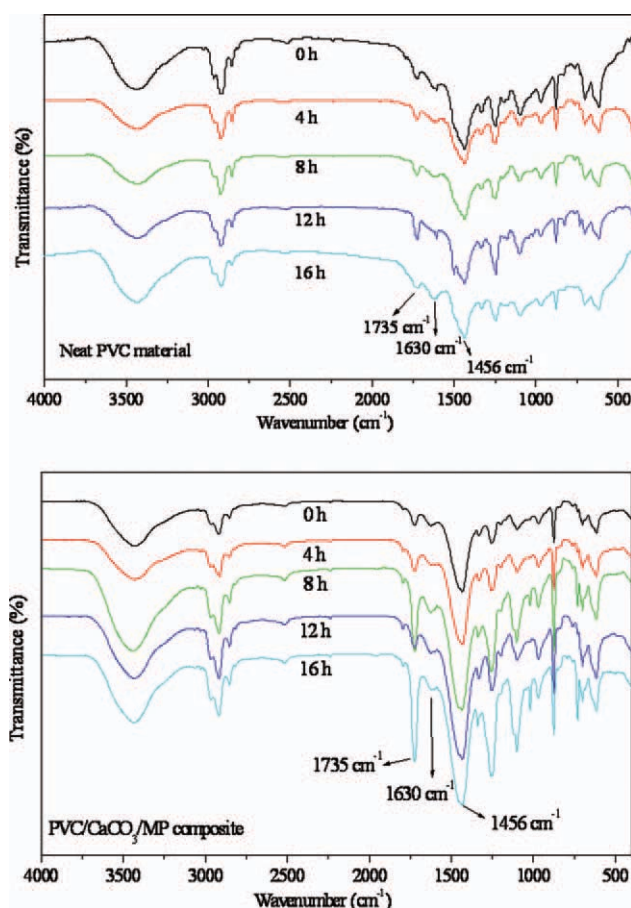
**Figure 4.** FTIR spectra of PVC/CaCO$_3$ and PVC/CaCO$_3$/MP composites in different irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as ultraviolet light screening agents in PVC matrix.[17,18] The inorganic fillers can absorb or reflect ultraviolet light, then form a barrier between polymer and light source. The barrier can prevent the UV light from the inside of polymer, and protect polymer matrix from the sun. Some research showed that CaCO$_3$ particles could reflect the ultraviolet light. It should play a protection role on the photo-degradation of polymers.[19] In addition, the antiaging properties of PVC resins are also influenced by the dispersion of inorganic fillers in PVC matrix. The inorganic fillers could effectively absorb or reflect ultraviolet light when they are uniformly dispersed in PVC matrix. The agglomerated inorganic fillers result in many defects of PVC matrix.

Based on these premises, it is reasonable to conclude that nano-CaCO$_3$ particles play the role of ultraviolet light screening agents in PVC matrix, and enhance the antiaging properties of PVC resins. In addition, due to the fairly good compatibility between MP and PVC matrix, the MP could significantly improve the compatibility of nano-CaCO$_3$ particles and PVC matrix. The good compatibility makes the inorganic fillers have fine dispersion in polymer matrix. So a small amount of modified nano-CaCO$_3$ particles added in the matrix could further enhance the composites antiaging time. Namely, the PVC/

CaCO$_3$/MP composite exhibits higher whiteness retention than PVC/CaCO$_3$ composite.

According to the GB-T5761-93, we definite the antiaging time $D_1$ and $D_2$, which represent the times as the whiteness retention achieves 70% and 60%, respectively. The high antiaging properties of the composites are dependent on the high values of $D_1$ and $D_2$. Figure 3 is the effect of nano-CaCO$_3$ particles contents on antiaging time $D_1$ and $D_2$ of PVC/CaCO$_3$ and PVC/CaCO$_3$/MP composites. It is found that both of the two kinds of composites aging times significantly increase along with the increasing contents of nano-CaCO$_3$ particles. As the dispersion of original nano-CaCO$_3$ particles in PVC matrix is not so good, the PVC/CaCO$_3$ composite antiaging time increased gently when nano-CaCO$_3$ particles content is less than 12 phr. When the content of nano-CaCO$_3$ particles achieves 16 phr, the mixed method in the process makes up the defects of bad dispersion. The antiaging time of PVC/CaCO$_3$ composite is obviously increased. When the nano-CaCO$_3$ is modified by MP, the compatibility with PVC matrix is improved. The modified nano-CaCO$_3$ has fine dispersion in PVC, and display excellent antiaging properties as ultraviolet light screening agent. It is specifically performed that a small amount of CaCO$_3$/MP addition
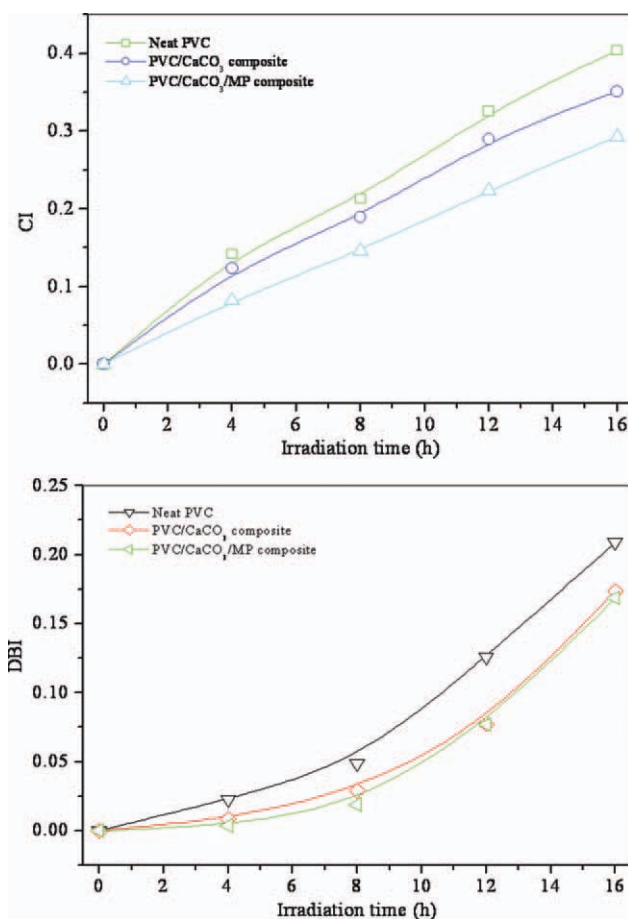


**Figure 5.** CI and DBI of neat PVC and two kinds of composites in different irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
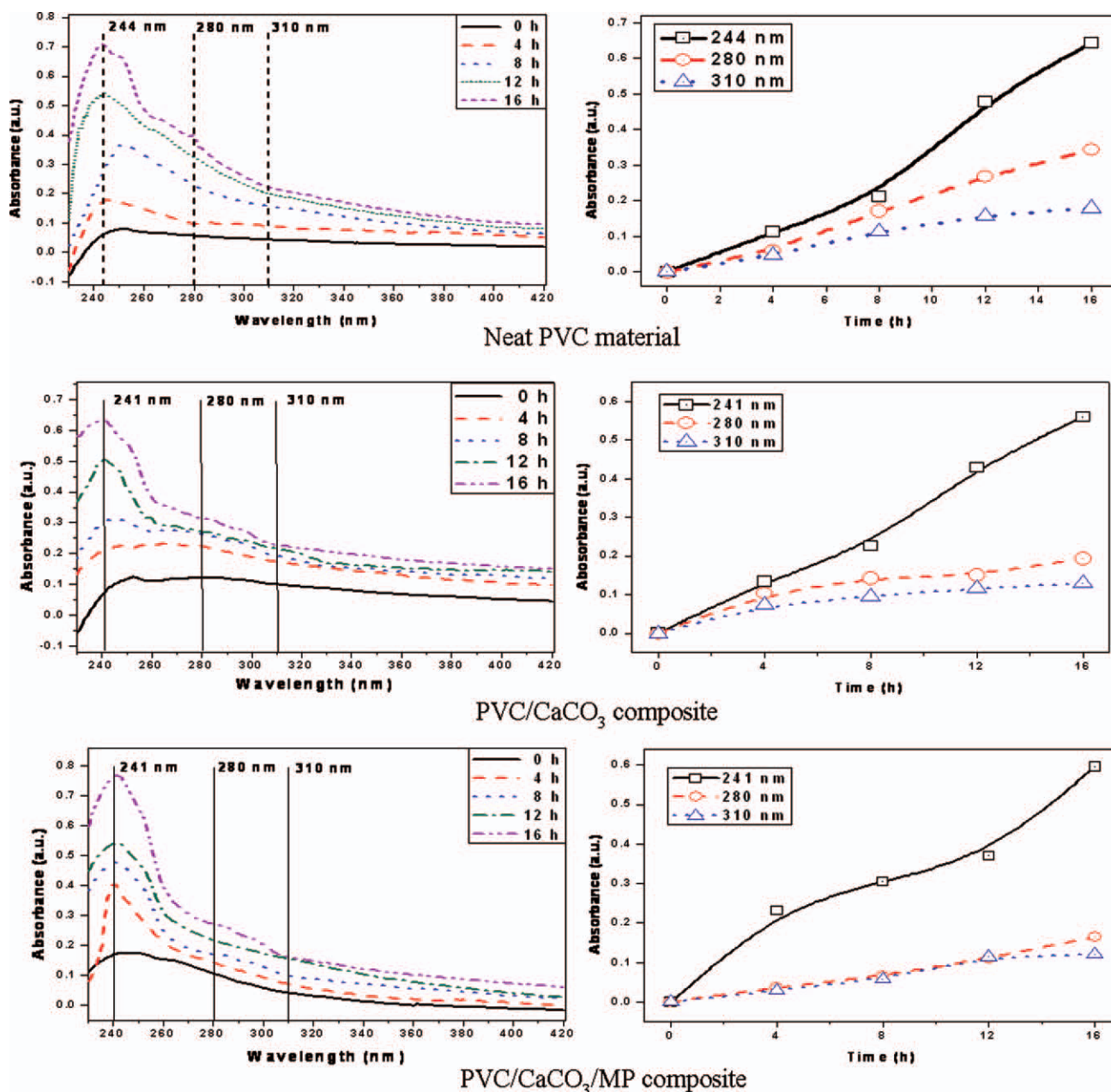
**Figure 6.** (Left) UV–vis spectra and (Right) absorbance variation with various wavelength of different PVC composites in continuous irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can significantly improve the PVC/CaCO₃/MP composite anti-aging time.

**FTIR Analysis**

Figure 4 shows the FTIR spectra of PVC/CaCO₃ and PVC/CaCO₃/MP composites at different irradiation times. The peak at 1456 cm$^{-1}$ is ascribed to the C—H bending vibration in PVC chain segment. The peak at 1630 cm$^{-1}$ is ascribed to the vinyl group of the hydrogen abstraction of PVC chains through the elimination of HCl molecules. And the peak at 1735 cm$^{-1}$ is ascribed to carbonyl group, which comes from the photo oxidation of PVC chains. The FTIR spectra of PVC/CaCO₃ and PVC/CaCO₃/MP composites all shows the characteristic peaks at

1630 cm$^{-1}$ and 1735 cm$^{-1}$. It demonstrates that the main degradation processes of photo degradation of rigid PVC are the dehydrochlorination and the simultaneous oxidation reactions. The carbonyl index (CI) and double bond index (DBI) are calculated by the infrared spectra change with the aging time, which is showed in Figure 5.

In Figure 5, the DBI and CI of the PVC/CaCO₃/MP composite are lower than that of PVC/CaCO₃ composite at the same aging time. Because the modified nano-CaCO₃ particles can uniformly disperse in PVC matrix and achieve good interfacial adhesion, which contribute to block ultraviolet light from the outside of the composites matrix and slow down the aging process.
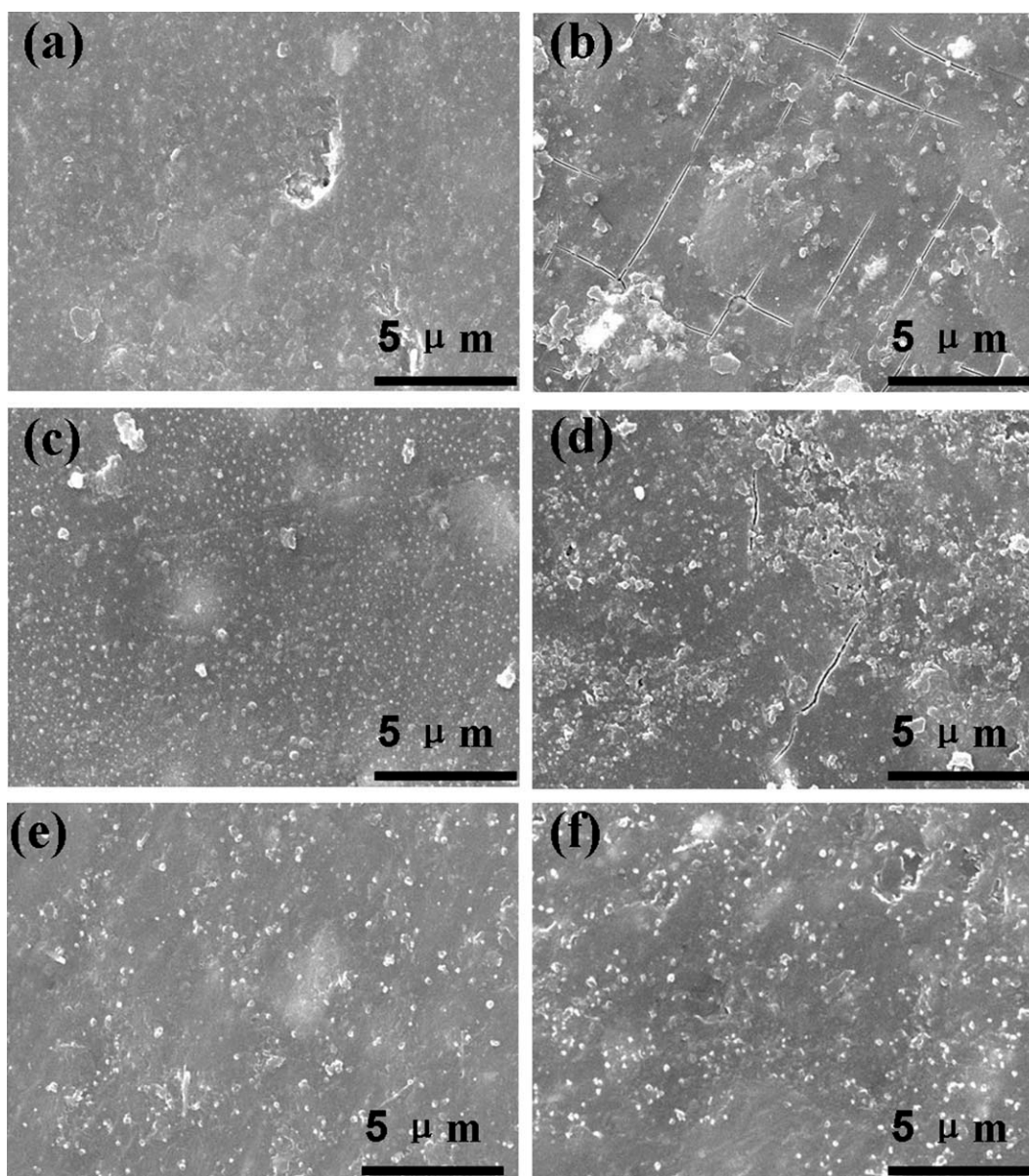
**Figure 7.** Surface SEM micrographs of composites in different aging time: neat PVC [(a) 6 h, (b) 12 h], PVC/CaCO$_3$ composite [(c) 6 h, (d) 12 h] and PVC/CaCO$_3$/MP composite [(e) 6 h, (f) 12 h].

### UV–vis Analysis

Figure 6 is the UV–vis absorbance of neat PVC, PVC/CaCO$_3$, and PVC/CaCO$_3$/MP composites after different irradiation times. It is obvious that ultraviolet absorption values of all composites increase with the aging time in the ultraviolet light region (wavelength for 220–420 nm). It means that the chromophoric groups, such as conjugated double bond and carbonyl groups, generate in the photo-oxidation process, and increase with the photo-oxidation continuously. The effect of irradiation time on absorption value variations of neat PVC and two kinds of PVC composites are shown in the right side of Figure 6. It is apparent that the addition of nano-CaCO$_3$ particles is effectively inhibited the growth speed of double bond, conjugated double bond and triple bond, corresponding to the 240, 280, and 310 nm in the left side of Figure 6, respectively. It is explained that

the addition of nano-CaCO$_3$ particles play a role of ultraviolet light screening agents. In addition, the growth speed of double bond, conjugated double bond and triple bond of the PVC/CaCO$_3$/MP composite are also lower than that of the PVC/CaCO$_3$ composite. It means that the modified nano-CaCO$_3$ particles have better antiaging properties than original nano-CaCO$_3$ particles.

### Surface Morphology Analysis

Figure 7 shows the SEM micrographs of neat PVC, PVC/CaCO$_3$, and PVC/CaCO$_3$/MP composites after irradiation for 6 and 12 h. It is seen that neat PVC, PVC/CaCO$_3$, and PVC/CaCO$_3$/MP composites surfaces appear more lightspots when these materials exposure to ultraviolet light for 6 h. The appeared lightspots are activation points formed in aging degradation. They are sensitive to stress and lead to the linear
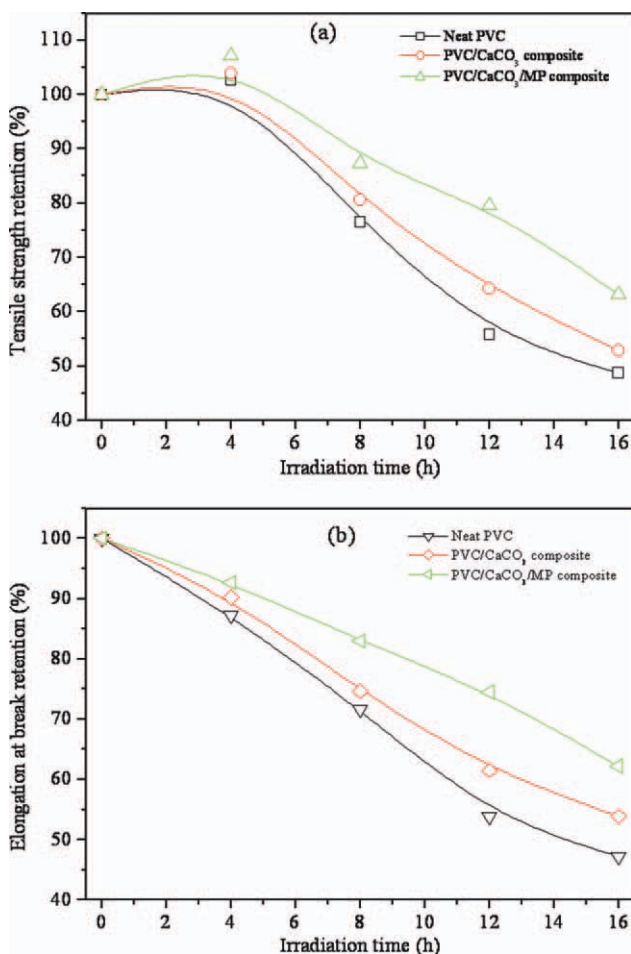
**Figure 8.** (a) Tensile strength retention and (b) elongation at break retention of neat PVC, PVC/CaCO₃ and PVC/CaCO₃/MP composite at various irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease of these materials mechanical properties. After irradiation for 12 h, due to continuous dehydrochlorination and oxidation reactions in the aging degradation, there are many cracks on the surface of neat PVC and PVC/CaCO₃ composite. However, the cracks on the surface of PVC/CaCO₃/MP composite are unobvious. In addition, the obvious cracks on the surface of PVC/CaCO₃ composite are fewer than that of neat PVC.

Obviously, these results suggest that the addition of nano-CaCO₃ particles has a significant influence on the antiaging properties of PVC resins. As evidenced by whiteness analysis discussed in a previous section and the unobvious cracks on the surface of the PVC/CaCO₃/MP composite, it is reasonable to infer that the modified nano-CaCO₃ particles has the best anti-aging properties in all of the materials.

**Mechanical Properties**

The aging time effect on tensile strength and elongation at break retentions of neat PVC and two kinds of PVC composites at 8 phr nano-CaCO₃ particles are shown in Figure 8. It is known that the tensile strengths of neat PVC and the two kinds of composites increase at the beginning of aging time. Then

they begin to drop gradually with the aging time increasing. It is mainly because the crosslinking reaction of conjugated double bond occurs in molecular chain during the early ultraviolet photoaging. The orientation stretching of PVC molecular chain becomes relatively difficult because of the significant increase of crosslinking structure. So the tensile strengths of the neat PVC and the two kinds of composites increase in the early stage of aging. Along with the increase of aging time, PVC degradation speeds up under the ultraviolet irradiation. The conjugated double bond and carbonyl groups in the molecular chain increase rapidly, which results in a large number of defects on the surface of composites. The tensile strength and elongation at break of neat PVC and two kinds of PVC composites decrease subsequently.

In addition, in the whole photoaging stage, PVC/CaCO₃/MP composite keeps better retention than neat PVC and PVC/CaCO₃ composite at tensile strength and elongation at break. After ultraviolet irradiation for 12 h, the PVC/CaCO₃/MP composite retention of tensile strength and elongation at break are 79.5% and 74.5%, far higher than that of PVC/CaCO₃ composite and neat PVC, while the tensile strength and elongation at break retention of the PVC/CaCO₃ composite and neat PVC are 64.2%, 55.8% and 61.5%, 53.9%, respectively. This indicates that the addition of modified CaCO₃ particles could improve the composite antiaging performance.

The aging time effect on impact strength retentions of neat PVC and two kinds of PVC composites at 8 phr nano-CaCO₃ particles are shown in Figure 9. It is obviously that the impact strengths of neat PVC and the two kinds of composites have slight variations when the aging time is less than 4 h. With the aging time increasing, the impact strengths of neat PVC and the two kinds of composites begin to decline gradually. It is not clear that what accounts for these behaviors. Presumably for two reasons: Firstly, ultraviolet photo-oxidation creates stress concentration points on the sample's surface. The oxidative degradation reaction on surface layer leads to physical defects in
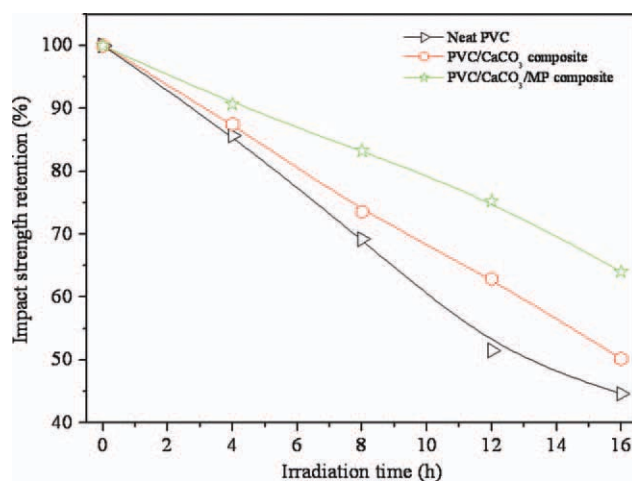


**Figure 9.** Impact strength retention of neat PVC, PVC/CaCO₃, and PVC/CaCO₃/MP composites at various irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite surface and forms stress concentration point during aging process. Under the effect of external stress, the stress concentration positions are easily to cause brittle fracture, depriving of the toughness and impact resistance performance. Secondly, photo-oxidation forms a brittle layer on the surface of PVC matrix, which also leads to the loss of toughness. So the impact strengths of the composites decrease along with the aging time increasing. In addition, in the photo-oxidation process, PVC/CaCO$_3$/MP composite impact strength retention is higher than that of neat PVC and PVC/CaCO$_3$ composite. For instance, after ultraviolet irradiation for 12 h, the impact strength retention of neat PVC and PVC/CaCO$_3$ composite are 51.5% and 62.9%, while the impact strength retention of PVC/CaCO$_3$/MP composite achieves 75.3%, improved by 46.2% and 19.7% than neat PVC and PVC/CaCO$_3$ composite, respectively. Therefore, it is concluded that the addition of modified nano-CaCO$_3$ particles into composite system obviously enhance the antiaging performance.

## CONCLUSIONS

From the above results, the following results can be concluded:

1. Nano-CaCO$_3$ particles and the macromolecule modified nano-CaCO$_3$ particles used as ultraviolet light screening agents could effectively improve the antiaging properties of PVC matrix. The mechanism is that the nano-CaCO$_3$ particles could reflect ultraviolet for destroying of PVC chain, and restrain dehydrochlorination and the simultaneous oxidation reactions.

2. Due to the modifying macromolecular around nano-CaCO$_3$ particles surface, the compatibility of nano-CaCO$_3$ particles and PVC matrix is significantly improved. The modified nano-CaCO$_3$ particles could uniformly disperse in PVC matrix and effectively reflect ultraviolet light. Based on these premises, the modified nano-CaCO$_3$ particles have better antiaging properties than nano-CaCO$_3$ particles for PVC matrix. The PVC/CaCO$_3$/MP composite has higher whiteness retention and lower CI and DBI than PVC/CaCO$_3$ composite.

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