

# The Mechanism for Inorganic Fillers Accelerating and Inhibiting the UV Irradiation Aging Behaviors of Rigid Poly(vinyl chloride)

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**ABSTRACT:** The UV irradiation aging behaviors of PVC composites with several inorganic fillers were studied through Fourier transform spectroscopy (FTIR), ultraviolet spectroscopy (UV-Vis), differential scanning calorimeter (DSC), scanning electron microscopy (SEM), and mechanical property test. It was found that incorporation of a small amount of the inorganic fillers such as CaCO<sub>3</sub>, talc and SiO<sub>2</sub> could hold up the UV aging behaviors of PVC. Those filler-filled PVC composites sheets after 20 days UV irradiation maintain lower carbonyl index (CI) and good appearance of surfaces, as compared with the corresponding neat PVC sheets, ascribed to high reflection of those fillers to UV light. While montmorillon-

ite (MMT) and pyrophyllite fillers could accelerate the UV aging behaviors of PVC, which could be concluded from both the sharp increase of the CI and lower  $T_g$  due to the chain scission reactions because of their high absorbance of these fillers to UV light in 290–400 nm. In these two PVC composites, UV irradiation caused the deterioration of their mechanical properties and the appearance of rough, cracked and chalked surfaces after 20 days UV irradiation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2869–2875, 2011

**Key words:** inorganic fillers; poly(vinyl chloride); aging behaviors

## INTRODUCTION

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.<sup>1,2</sup> Simultaneously, oxygen will interfere with the various photochemical processes involved and thus is responsible for the production of such photosensitive structures as hydroperoxide or carbonyl groups. Afterwards, the peroxide crosslinking and chain scissions occur in the photooxidation of PVC as a result of the various reactions of the peroxy radicals. All these chemical changes lead to the deterioration of the mechanical properties of PVC.

Moreover, as photo-degradation is primarily a superficial process due to the limited penetration of UV irradiation and the oxygen starvation in the center of the samples, the surface properties of the degraded PVC materials are substantially changed as shown by the observed loss of abrasion resistance, gloss, and interfacial free energy.<sup>3–8</sup>

In PVC composites, inorganic fillers, such as mica, talc, CaCO<sub>3</sub>, are often used to improve the mechanical properties of PVC and decrease its cost.<sup>9</sup> Further, inorganic fillers can also enhance flame retardancy, thermal stability, and barrier performance of PVC.<sup>10–14</sup>

Since inorganic fillers have generally played an important role on the industrial applications of PVC and are of high reflection to light, their effects on the photo-degradation of PVC should not be neglected. Day et al.<sup>15</sup> mentioned that the strong absorption of most harmful wavelengths in solar radiation of titanium dioxide (TiO<sub>2</sub>) resulted in the protection of the polymer matrix from photochemical degradation. Gesenhues et al.<sup>16</sup> found that TiO<sub>2</sub> was not photo-catalytically active in dry irradiation of PVC, while the photooxidation of TiO<sub>2</sub>-pigmented PVC became much faster during weathering at the same intensity. Unfortunately, the studies are mainly focused on TiO<sub>2</sub>, while the effects of other inorganic fillers do not attract enough attentions. Shnchez-Solis

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et al.<sup>17</sup> reported that by adding mine sand the decrease in mechanical properties of PVC composites could be prevented after irradiation. Zaharescu et al.<sup>18</sup> mentioned that mica plays a role of absorbent for hydrochloric acid formed by PVC irradiation, and tensile strength, volume resistivity and loss factor results prove that PVC/mica may be used as electrical insulator. Recently, Essawy et al.<sup>19</sup> found that the stabilization ability of laponite to UV irradiation of PVC was attributed to both scattering the incident light and trapping a growing radical.

To investigate the effects of inorganic fillers on the UV irradiation aging behaviors of PVC, general inorganic fillers such as calcium carbonate (CaCO<sub>3</sub>), talc, silicon dioxide (SiO<sub>2</sub>), montmorillonite (MMT), and pyrophyllite were chosen. The morphology and properties development of PVC composites, including carbonyl index, glass transition temperature, surface appearance, and mechanical properties were discussed. On the basis of the relative absorbance of these fillers to UV light in 290–400 nm, the mechanism for these inorganic fillers accelerating and inhibiting UV aging behaviors of PVC was proposed.

## EXPERIMENTAL

### Materials

PVC, SG-8 with a number-average molecular weight of  $5.0 \times 10^4$ , Jinlu Group, Sichuan, China. Tribasic lead sulfate and dibasic lead phosphate, Tianshen Plastic Auxiliary, Zhejiang, China. Stearic acid, Kelong Chemical Reagent Plant, Sichuan, China. CaCO<sub>3</sub>, Lanhua Huaming Nanometer Mineral, Shanxi, China. Talc, Chengdu Qiuqiang Powder Making, Sichuan, China. SiO<sub>2</sub>, Guangdong Haihua Chemical, Guangdong, China. MMT, Southern Clay Products, USA. Pyrophyllite, Hongyuan Powder Making, Zhejiang, China.

### Sample preparation

One hundred parts of PVC, inorganic filler (powder, 1 phr), tribasic lead sulfate (powder, 2 phr), dibasic lead phosphite (powder, 1 phr), and stearic acid (powder, 0.5 phr) were dry blended. The mixture was milled by an open twin roller at 170°C for a period of 5 min. The compressed PVC sheet, with ~1.0 mm thickness, was prepared. Dumbbell shaped samples with dimension of  $25 \times 4 \times 1 \text{ mm}^3$  for tensile property measurement were cut from the PVC sheets. The surface layer from the irradiated samples was used to the FTIR and DSC measurements.

### Accelerated ultraviolet-weathering tests

Accelerated artificial UV-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  $5.5 \text{ W/m}^2$  at 340 nm. The accelerated irradiation test was completed after 480 h (total time).

### Measurements and characterization

The infrared spectra of samples were obtained by using a Nicolet 560 Fourier Transform Infrared (FTIR) Spectrometer. The  $2915 \text{ cm}^{-1}$  peak, which was attributed to the stretching vibration of C–H, was selected as an internal reference. The carbonyl index (CI) was defined to show the photooxidation degree of the material and the formation of the vinyl group was characterized by the vinyl index (VI):

$$\text{CI} = A_{\text{C=O}}/A_{2915}$$

$$\text{VI} = A_{\text{C=C}}/A_{2915}$$

Where,  $A_{\text{C=O}}$  is the peak area of carbonyl group,  $A_{\text{C=C}}$  is the peak area of vinyl group, and  $A_{2915}$  is the peak area of C–H.

The UV spectra of samples were collected by a Hitachi U-3310 ultraviolet-visible spectrophotometer in the wavelength range of 240–800 nm. The UV ratio is defined to determine the UV absorbance ratio in the whole light range measured:

$$\text{UV}\% = A_{290-400}/A_{290-800}$$

Where,  $A_{290-400}$  is the area of the absorbance curves at the range of 290–400 nm and  $A_{290-800}$  is the area of the absorbance curves at the range of 290–800 nm. Here the effective UV light for the photo-degradation of PVC composites is in the range of 290–400 nm.

The surface morphological images of different PVC sheets before and after irradiation were taken by SEM (JSM-5900LV, Electron Optics Laboratory, Japan). Before the observation, the surfaces were deposited by Au. The accelerating voltage was 20 kV.

DSC measurements were performed by TA DSC 204 to investigate the glass transition temperature changes of PVC during irradiation. All tests were performed in nitrogen atmosphere. For each test, the sample was heated from 40 to 100°C at a rate of 10°C/min and then maintained at 100°C for a period of 3 min to ensure an identical thermal history. The specimen was subsequently cooled down to 40°C quickly. Then the sample was heated from 40 to 120°C at a rate of 10°C/min.

The tensile property tests were carried out on a SANS CMT4104 testing machine at a strain rate of 20 mm/min at 23°C and measurements were made on at least five specimens of each sample.

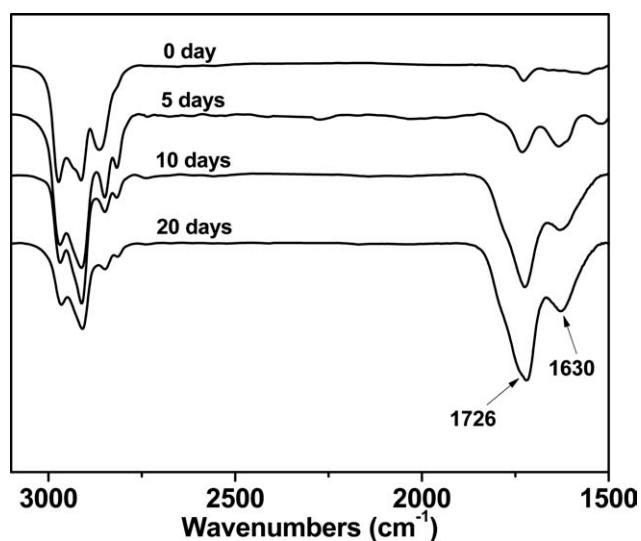


Figure 1 FTIR spectra of neat PVC irradiated for different days.

## RESULTS AND DISCUSSION

The IR spectra of neat PVC during UV irradiation process are shown in Figure 1. Significant change occurs after three days irradiation. The characteristic bands at 1630 and 1726  $\text{cm}^{-1}$  are attributed to vinyl and carbonyl groups, respectively. The corresponding intensities increase gradually with irradiation time. Here the vinyl group comes from the hydrogen abstraction of PVC chains through the elimination of HCl molecules. The carbonyl group comes from the photo oxidation of PVC chains. It demonstrates that the main degradation processes of photo degradation of rigid PVC are the dehydrochlorination and the simultaneous oxidation reactions. The photo degradation mechanism of PVC can be summarized in Figure 2. The upper cycle corresponds to the dehydrochlorination which is slightly affected by the

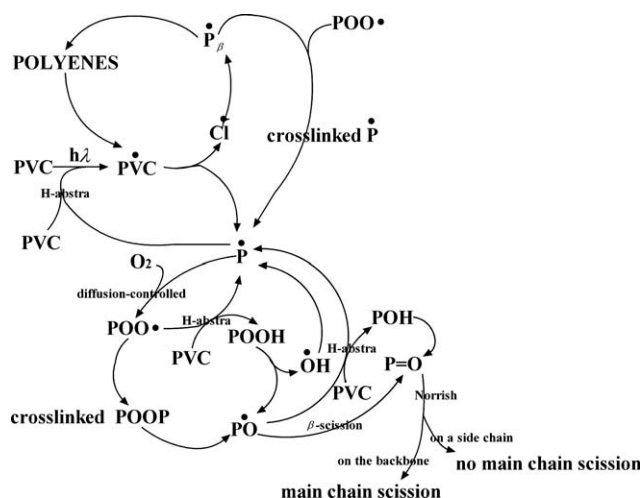


Figure 2 Schematic representation of the photodegradation process of PVC.

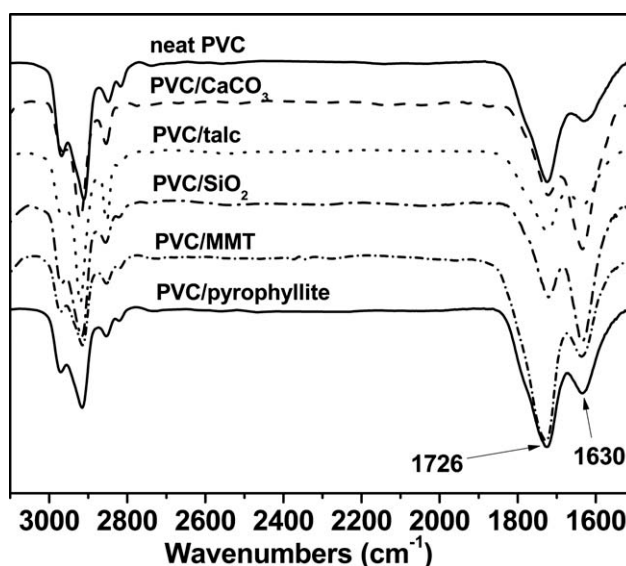


Figure 3 FTIR spectra of neat PVC and PVC composites after 20 days irradiation.

presence of  $\text{O}_2$ . The result is the formation of HCl and the conjugated polyene sequences, which is responsible for the discoloration of the irradiated PVC. The oxidation process is represented by the lower cycle which includes several chain reactions. In the presence of oxygen, alkyl radicals can be scavenged by  $\text{O}_2$  and lead to the formation of relatively lower activated peroxy and alkoxy radicals.<sup>1,2</sup> And the following hydrogen abstraction reactions of these radicals result in the formation of oxygenated structures on the PVC backbone. These oxygenated structures eventually initiate the chain scission and crosslinking reactions.

For different inorganic fillers filled PVC composites, the degradation degrees are different. The degradation degrees of PVC/MMT and PVC/pyrophyllite are much higher than those of PVC/ $\text{CaCO}_3$ , PVC/talc and PVC/ $\text{SiO}_2$ , as shown in Figure 3. To further describe this process, carbonyl index and vinyl index are used to investigate the aging behaviors of fillers-filled PVC composites.

The effects of these fillers on the change of carbonyl indexes (CI) during irradiation are shown in Figure 4. In PVC/ $\text{CaCO}_3$ , PVC/talc and PVC/ $\text{SiO}_2$ , the change of carbonyl index is relatively slow during irradiation, indicating that these fillers could hinder the photo-oxidation of PVC. However, in PVC/MMT and PVC/pyrophyllite, a sharp increase of CI is observed with irradiation time. These two inorganic fillers have great impact on the oxidation and play more negative roles on the aging behaviors of PVC. From Figure 4, the fillers can be ranked based on their acceleration effects on photo-oxidation of PVC as: MMT > pyrophyllite > talc >  $\text{SiO}_2$ ,  $\text{CaCO}_3$ .

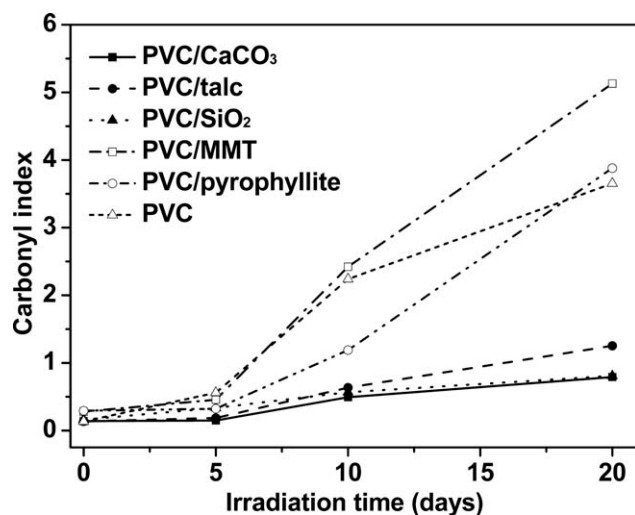


Figure 4 Change of carbonyl groups during irradiation of neat PVC and PVC composites.

Figure 5 shows the change of concentration of vinyl groups during irradiation of PVC and PVC composites. For all the PVC composites, the formation of vinyl groups increases with irradiation, but there is still a little difference with that of carbonyl groups. As mentioned in Figure 2, vinyl group is mainly obtained through dehydrochlorination reaction, while carbonyl group is formed through oxidation reaction. From Figures 4 and 5, it can be concluded that different fillers play different roles on these two reactions. The fillers, such as CaCO<sub>3</sub>, talc and SiO<sub>2</sub>, promote the formation of vinyl groups. MMT and pyrophyllite fillers restrain the formation of vinyl groups, while they promote the formation of carbonyl groups.

To reveal why various fillers have different effects on the photo-degradation of PVC, ultraviolet analy-

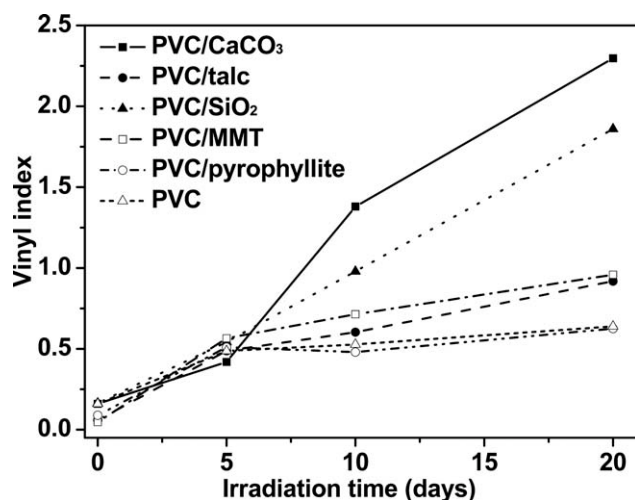


Figure 5 Change of vinyl groups during irradiation of neat PVC and PVC composites.

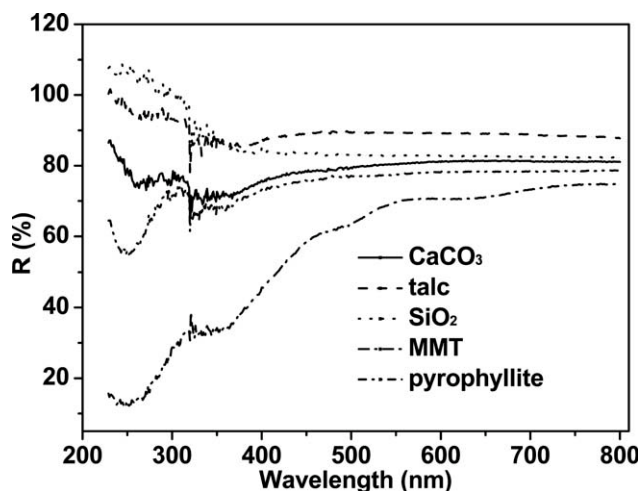


Figure 6 The ultraviolet reflections of inorganic fillers.

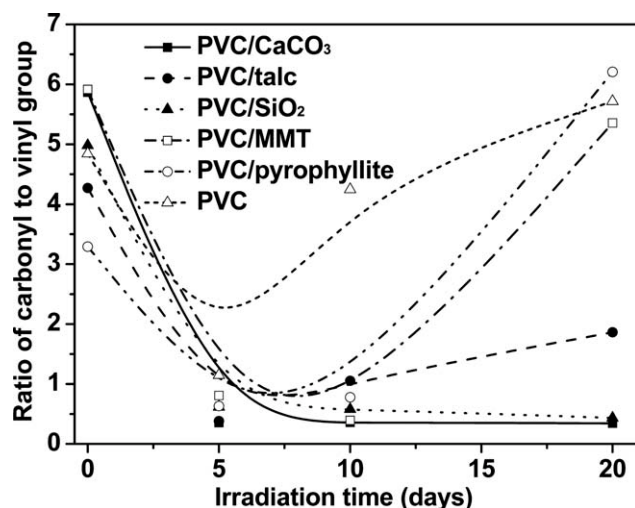
ses are used to investigate the reflections of these inorganic fillers to the UV light. It is well known that the light ranging from 290 nm to 400 nm mainly causes the photo-degradation of polymers (the light with the wavelength lower than 290 nm is filtered by the air). In general, light absorbers could prevent polymers from being degraded by the UV light through absorbing light in this range. On the other hand, if inorganic fillers could reflect the UV light, they should play a protection role on the photo-degradation of polymers. However, few studies focused on the effects of inorganic fillers.

The reflections of these inorganic fillers to light at the range of 290–800 nm are shown in Figure 6. The lower the reflection ratio, the more the inorganic filler absorbs UV light, and *vice versa*.<sup>20</sup> The results show that CaCO<sub>3</sub>, talc and SiO<sub>2</sub> have high reflection ratios which are up to 80%. The other fillers which accelerate the photo-oxidation degradation of PVC have relatively low reflection ratios. Comparing this result with the CI changes, it could be concluded that CI changes depend on the reflection ratios of the fillers to the ultraviolet light ranging from 290 nm to 400 nm. The UV ratios (UV%) of inorganic fillers are listed in Table I. It is clear that the order of relative absorbances of inorganic fillers to UV light from top to bottom accords quite well with the order of CI changes. This result proves that the reflection of

TABLE I  
UV Absorbance of Inorganic Fillers

Inorganic filler	UV %
CaCO <sub>3</sub>	23.4
Talc	18.2
SiO <sub>2</sub>	15.7
MMT	68.3
pyrophyllite	30.6





**Figure 7** Change of ratio of carbonyl to vinyl index during irradiation of neat PVC and PVC composites.

ultraviolet light is a predominant factor in the photo-degradation process of PVC composites.

Further, in our point of view, developments of carbonyl index and vinyl index are related with the catalysis of inorganic fillers to the oxidation reactions of PVC composites after the absorption of the UV irradiation. Figure 7 gives the change of ratios of carbonyl to vinyl index during irradiation. From this change, the degrading routines of PVC and PVC composites can be clearly observed. In PVC, PVC/MMT and PVC/pyrophyllite, dehydrochlorination reactions are relatively serious at the early irradiation. From gradual increase of this value after five days irradiation, it is found that oxidation reactions gradually predominate with the irradiation time. However, in PVC/CaCO<sub>3</sub>, PVC/talc and PVC/SiO<sub>2</sub>, dehydrochlorination reactions predominate during the irradiation, even at the end of irradiation these ratios still keep invariable. These indicate that inorganic fillers would significantly change the photo-degradation processes of PVC, especially in the presence of oxygen. MMT and pyrophyllite would trigger the scavenging of oxygen, they can also screen the UV light at a certain degree. Oxygen could readily react with the unstable transients arising by UV irradiation, either by deactivating the excited states (quenching reaction) or by combining with free radicals to form peroxy radicals (scavenging reaction) as follow:



By deactivating the excited polyene sequences formed during the UV irradiation of PVC, the quenching reaction should reduce the extent of the dehydrochlorination. Conversely, the scavenging reaction is expected to start an autooxidation process and thus to be responsible for the oxidation products. The relative importance of these two reactions during the photo-degradation of PVC in the presence of oxygen depends primarily on the fillers. MMT and pyrophyllite play an important role on the scavenging process and induce the oxidation reaction, while others retard this reaction.

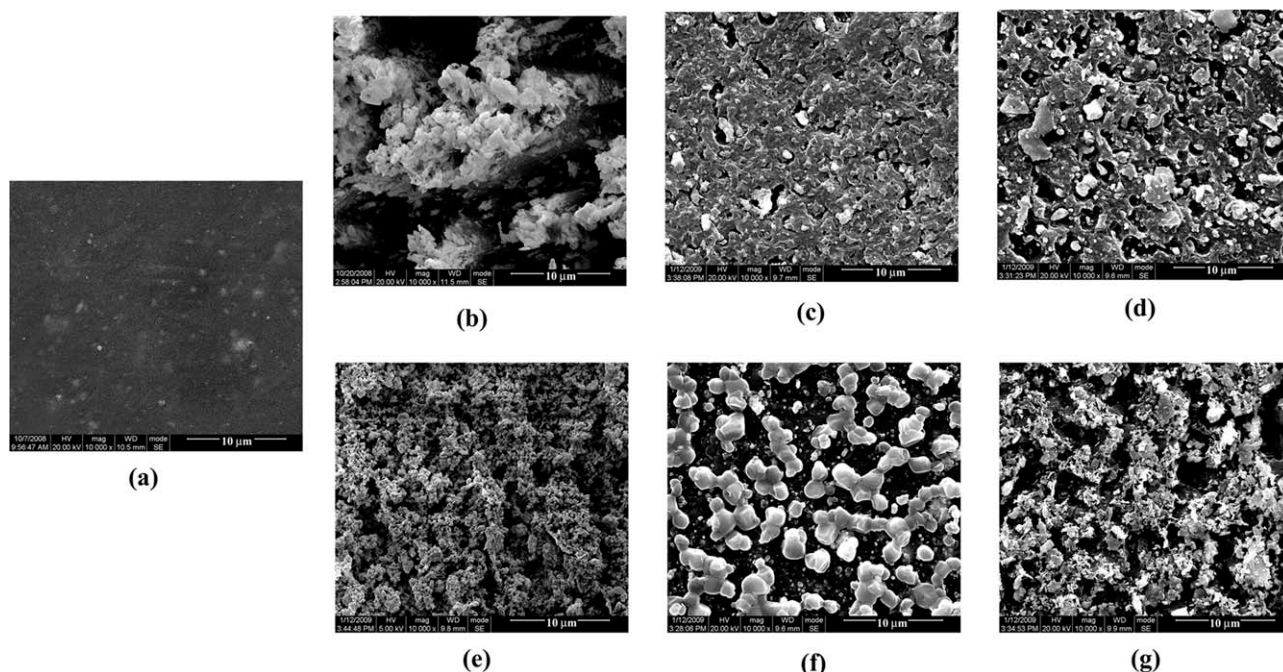
DSC analyses can be used to identify the change of irradiated surface. Glass transition temperatures ( $T_g$ ) of PVC and fillers filled PVC composites during UV irradiation process are shown in Table II.  $T_g$  of neat PVC decreases to 82.7°C from 84.0°C after 20 days irradiation. This can be explained by both the formation of short chains and the totally chalked surface during irradiation.

In PVC/CaCO<sub>3</sub>, PVC/talc, and PVC/SiO<sub>2</sub>, after 20 days irradiation,  $T_g$  values are slightly greater than those of unirradiated ones. This can be explained by the existence of conjugated polyene sequences. From Figure 5 it can be seen that the increase of vinyl groups in PVC/CaCO<sub>3</sub>, PVC/talc, and PVC/SiO<sub>2</sub> is more significant than that of others, and the increase of vinyl groups (conjugated polyene sequence concentration) facilitates the rigidization of PVC chains, eventually leading to the increase of  $T_g$ . Meanwhile, in PVC/MMT and PVC/pyrophyllite,  $T_g$  decreases with irradiation time, from 84.2 to 81.9°C and from 83.5 to 82.3°C, respectively. The shift of  $T_g$  to lower temperature is attributed to a plasticization of the low-molecular weight products resulting from an efficient bond cleavage process induced by the carbonyl groups.

What should be emphasized here is that though main chain scission and crosslinking reactions occur simultaneously during the photodegradation of polymer, which one is predominated process depends on the photo-degradation mechanism of irradiated PVC or PVC composite.<sup>20,21</sup> So from the DSC results it can be concluded that inorganic fillers play an important role on the photodegradation of

**TABLE II**  
 $T_g$  Changes of PVC and PVC Composites Irradiated for Different Days

Irradiation time (day)	Neat PVC	PVC/CaCO <sub>3</sub>	PVC/talc	PVC/SiO <sub>2</sub>	PVC/MMT	PVC/pyrophyllite
0	84.0	83.9	83.4	84.1	84.2	83.5
5	83.9	84.0	84.0	84.2	83.8	83.9
10	83.7	84.0	84.5	84.5	83.3	83.3
20	82.7	85.8	84.4	84.9	81.9	82.3



**Figure 8** The surface changes of PVC filled with different fillers before and after 20 days irradiation ( $\times 10,000$ ). (a) PVC before irradiation; (b) PVC after irradiation; (c)–(g) PVC composites after irradiation. (c) PVC/ $\text{CaCO}_3$ ; (d) PVC/talc; (e) PVC/ $\text{SiO}_2$ ; (f) PVC/MMT; (g) PVC/pyrophyllite.

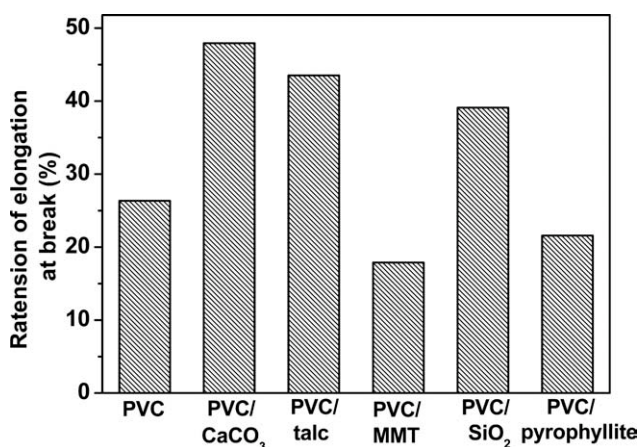
PVC as both screening agents and modifiers of photo-degradation route, eventually determining the predominant reaction during the whole photo-degradation process.

SEM analyses on the surface of PVC composites before and after irradiation are carried out to understand the influence of surface change on the photo-degradation of PVC. It is widely accepted that the oxygen plays an important role on the photo-degradation of polymer. The degradation usually begins from the surface and then develops along the depth gradually.<sup>17,23</sup> Hence the surface pattern has a direct influence on the bulk degradation of the material. If the surface destruction is slight, the oxidation will

be constrained to a very thin layer at the surface. Alternatively, a serious oxidation surface supplies more opportunities for the oxygen to diffuse into the interior, thus causing further oxidation of the bulk, till the material breaks down.

Figure 8 shows comparisons between samples before and after irradiation. Before irradiation, the sample surfaces are relatively smooth, except for some defects coming from the compression molding [Fig. 8(a)]. After 20 days, the surface of neat PVC is totally chalked and this chalked surface is caused by the serious chemical reactions such as dehydrochlorination, oxidation, and chain scission due to the high irradiation intensity. While for -filled PVC composites, there are more or less cracks and fillers exposed to the surface after 20 days irradiation. PVC/pyrophyllite composites have rough surfaces, with big and deep cracks. At the surface of PVC/MMT composites, many white particles can be observed, which indicated that PVC around MMT particles totally disappeared. In PVC/ $\text{CaCO}_3$ , PVC/talc and PVC/ $\text{SiO}_2$ , the surface damages are somehow slighter. There are only a few of small cracks on the surfaces.

The mechanical properties of PVC and PVC composites in terms of elongation at break are measured before and after irradiation. Figure 9 shows the variation of the retention of elongation at break after 20 days irradiation. The neat PVC shows a sharp loss in the elongation at break. PVC/ $\text{CaCO}_3$ , PVC/talc, and PVC/ $\text{SiO}_2$  show a great resistance to deterioration in the mechanical properties. While PVC/MMT



**Figure 9** Change of the retention of elongation at break after 20 days irradiation.

and PVC/pyrophyllite yield worse resistance to the effects of UV radiation due to MMT and pyrophyllite accelerating the photo-degradation of PVC. It is well known that embrittlement of polymer during irradiation is usually attributed to chain scission.<sup>24</sup> When the molecular weight becomes lower than a critical value  $M_c$ , the entanglement network is destroyed, plastic deformation can not occur and the toughness decreases sharply by two or three orders of magnitude. Cracks propagate rapidly in the oxidized layer. After 20 days irradiation, the surface of neat PVC is totally chalked and the concentration of carbonyl groups greatly increases. Combining with the carbonyl index and the  $T_g$  value, it can be concluded that in PVC/CaCO<sub>3</sub>, PVC/talc, and PVC/SiO<sub>2</sub>, the chain scission reactions are relatively slow, indicating these fillers can retard the deterioration of mechanical properties. While in PVC/MMT and PVC/pyrophyllite, MMT and pyrophyllite accelerate this process due to the sharp chain scission reaction.

### CONCLUSIONS

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

1. Inorganic fillers have important effects on the photodegradability behaviors of PVC, and the behaviors mainly depend on the reflection capability of these fillers. Among the fillers studied, CaCO<sub>3</sub>, talc, and SiO<sub>2</sub> stabilize PVC to some extent. However, MMT and pyrophyllite act as photo-oxidation catalysts, accelerating the oxidation and chain scission processes, eventually leading to the increase of CI and the decrease of  $T_g$ , respectively.
2. Combining the FTIR, UV-Vis, DSC, SEM, and mechanical property test of the PVC composites, CaCO<sub>3</sub>, talc, and SiO<sub>2</sub> can reflect nearly all the ultraviolet light, holding up the oxidation and chain scission processes of PVC. Therefore, there are only a few cracks on the surface of these composites, and the surface damage is slight. In the PVC/MMT and PVC/pyrophyllite composites, a sharp shift of CI to

high value is observed, and the formation of short chains leads to the decrease of  $T_g$  value. Seriously damaged surface and deteriorated mechanical properties occur during UV irradiation.

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