

Effect of Vinyl Acetate on Aging Mechanism of Polyacrylate Under UV Light

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ABSTRACT: Diversity of aging behaviors of polyacrylate and poly(vinyl acetate-acrylate) with the ultraviolet light radiation was studied. The aging degree was evaluated and the mechanism dominated the behaviors was investigated by color aberration, the degree of cross-linking, molecular weight and its distribution by gel permeation chromatography (GPC), ultraviolet absorption spectroscopy (UV-vis), and fourier transform infrared spectrometer (FTIR). These studies found that although photodegradation mechanism of poly(vinyl acetate-acrylate) still preserves three main steps of the scission of main chain, formation of double bond and the generation of cross-linking reaction, introducing struc-

tural units of vinyl acetate to polyacrylate cause the rules various. The structural units can aggravate the aging of polyacrylate, through increasing formation of double bonds and generating cross-linking reaction. However, what is interesting is that the structural units can strikingly restrain main chain from scission. It is significant for modifying the photodegradation behaviors of polyacrylate coatings. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1717–1724, 2009

Key words: aging behaviors; polyacrylate; poly(vinyl acetate-acrylate); ultraviolet light; photodegradation mechanism

INTRODUCTION

Because of its good characteristics of film forming and mechanical properties, optical clarity, and overall stability, polyacrylate is widely used in the formulation of paints, surface coatings, and adhesives.¹

But, in practical application, with the effects of light, water, temperature, and their interaction, physical, chemical, and physical-chemical aging will take place in polymer materials. Particularly, the harmful effects from illumination to polymer materials mainly deal with ultraviolet light and oxygen, which can cause a series of complicated degradation reactions. Ultraviolet wavelengths mainly concentrate on 200–400 nm in which, some researches found, polymers tend to generate the following changes: (1) photo-oxidative degradation of polymers; (2) formation of double bonds; (3) degradation of peroxides; (4) formation of chromophore.²

The degradation of polyacrylate will affect the performance and the service life, especially when polyacrylate is used as coatings. Therefore, it has aroused more and more focuses on the research of

photo-degradation mechanisms. Chiantore et al.³ pointed that the acrylate units were more reactive towards oxidation, in comparison with the methacrylate ones. With short alkyl side groups chain scissions prevailed over cross-linking reactions both in acrylate and methacrylate samples. The degradation of poly(butyl methacrylate) proceeds in a completely different way, with extensive cross-linking and simultaneous fragmentation reactions. It also has been reported that under ultraviolet irradiation the main degradation pathway is chain scission, and rates of photodegradation of the different resins may be related to the type of ester group and to the presence of the α -methyl in the main chain.⁴

In addition, it is well known that the copolymerization of vinyl acetate with other monomers, such as methacrylate⁵ or acrylate,⁶ produces useful latexes having a wide range of properties. But poly(vinyl acetate-acrylate) has bad age-resistance compared with polyacrylate. Duquesne et al. researched the mechanism of degradation of vinyl acetate/butyl acrylate(VA/BA) copolymers varying the VA/BA ratio. It is shown that for higher VA contents, the degradation starts at comparatively lower temperature but a more thermally stable material is formed.⁷ So, the researches on how the structural units of vinyl acetate effect the polyacrylate are very interesting.

In this article, we adopt polyacrylate and poly(vinyl acetate-acrylate) with a little vinyl acetate as the

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studying objects, and accelerates their aging process under 254 nm ultraviolet radiation in the experiment. The research mainly determines the change of the molecular structure during the aging processes of polyacrylate and poly(vinyl acetate-acrylate) under ultraviolet radiation by fourier transform infrared (FTIR) spectrometer, gel contents and gel permeation chromatography (GPC). Comparing the two aging processes with each other, the research focuses on the synergies effect between structural units of vinyl acetate and acrylate in the copolymer, and furthermore means to ascertain the aging mechanism of polyacrylate during existence of poly(vinyl acetate) units. And the research obtains interesting results.

EXPERIMENTAL

Materials

Vinyl acetate (VAc, Tianjing Chemical Factory), methyl methacrylate (MMA, Shanghai Bodi Chemical Factory), butyl acrylate (BA, technical grade), potassium peroxydisulfate (Chengdu Kelong Chemical Factory), sodium dodecyl benzene sulfonate (SDBS, Chengdu Kelong Chemical Factory), acetone (Shanghai Institute of Organic Chemical Reagents), acetonitrile (Chengdu Kelong Chemical Factory), and tetrahydrofuran (Chengdu Kelong Chemical Factory), were used as received.

Sample preparation

All the polymerizations were carried out in a 250-mL three-neck flask equipped with a mechanical stirrer, return condenser and thermometer. In the experiment, BA, MMA, or VAc mixed with sodium dodecyl benzene sulfonate, which was emulsifying agents, and distilled water were all added into the flask in proportion. At the same time, the solution was heated by the water bath. The mixture was stirred to be completely pre-emulsified. When water bath was heated to 80°C or 60°C, the initiator potassium persulfate was added into the solution. And the reaction was kept for 4–6 h after the mixture appeared blue fluorescence. Then polyacrylate emulsion or poly(vinyl acetate-acrylate) emulsion would be produced. At last, the emulsion was put in the mold to get film under room-temperature. And the thickness of samples is 1 mm.

Measurements and characterization

The films of the samples were placed in the ultraviolet ray irradiation box, which was made by ourselves. Because the maximum ultraviolet absorption wavelength of polyacrylate is 246 nm, the wave-

length of the UV light was identified as 254 nm and the power was 28 W. Otherwise, the shape of the light is tubular. The distances between the films and the UV light were 15 cm, and the temperature in the aging box was 25°C. Under ultraviolet ray irradiation, a cycle-aging test lasted 48 h and each cycle has two samples. Then, the performance of the samples under different aging cycles was characterized.

The variety of chromatic aberration was tested by CM-2300d colorimeter made in Konica Minolta. The absorption spectra were determined by TU-1810 UV/Vis spectrophotometer using tetrahydrofuran as solvent.

FTIR spectra of samples before and after aging were investigated with Nicolet 560 FTIR spectrometer from 4000 to 600 cm^{-1} . The samples for measurements were dissolved by acetonitrile according to a certain concentration, and then the solution was spread in the flake of KBr. In order to analyze the changes of characteristic groups before and after aging, Lambert-Beer law was introduced. And utilizing deformation of the equation, quantitative analysis can be carried.

Lambert-Beer law

$$A = \lg I_0 I = \varepsilon lc$$

where A is absorbed intensity; I_0 is the incident light intensity; I is the transmission light intensity; ε is the absorption coefficient; l is the sample thickness; and c is sample concentration.

$$A_1 = \varepsilon_1 l_1 c_1$$

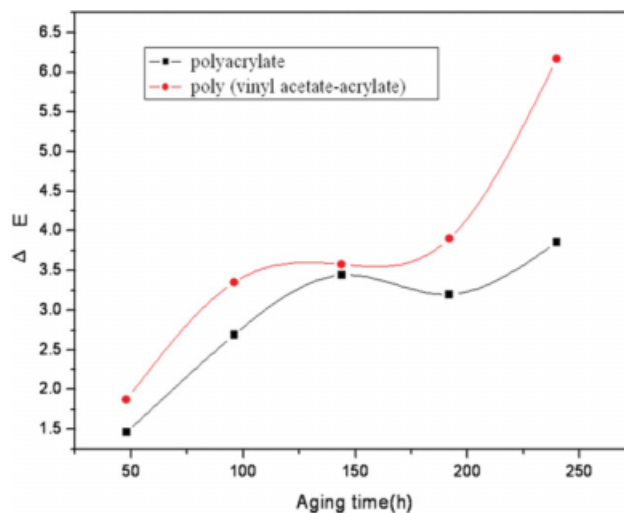


Figure 1 Changes of ΔE along with the aging time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

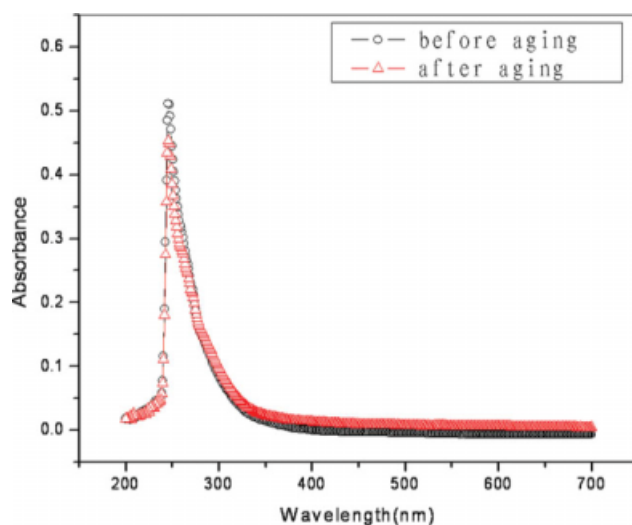


Figure 2 Ultraviolet absorption spectrums of polyacrylate before and after irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

$$A_0 = \varepsilon_0 l_0 c_0$$

$$A_1/A_0 = kc_1/c_0$$

The test of the gel content is carried out in Soxhlet extraction. The fragments of the films wrapped by filter were placed in Soxhlet extraction filled with acetone. After the bath pot was heated to 70°C, the samples were extracted for 48 h. Then the samples were taken out from Soxhlet extraction, and dried in a bake oven at 90°C and weighed. The formula of the gel content is as follows:

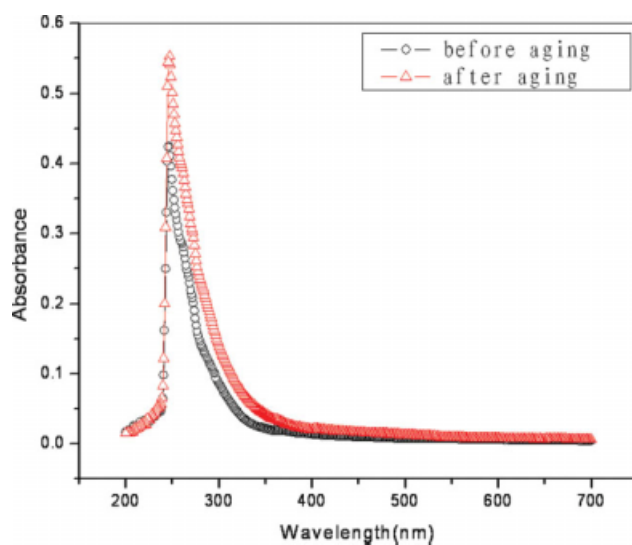


Figure 3 Ultraviolet absorption spectrums of poly(vinyl acetate-acrylate) before and after irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

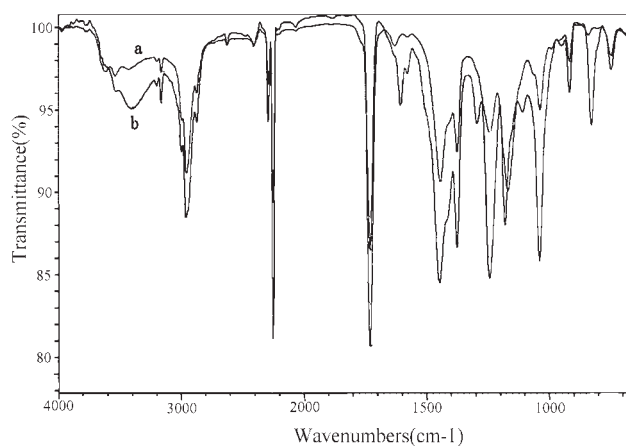


Figure 4 IR of polyacrylate before (a) and after (b) irradiation.

Percentage of the gel content

$$= (m_2 - m_0)/(m_1 - m_0) \times 100\%$$

where m_0 is the quality of the filter, m_1 is the quality of the filter and the sample before extraction, and m_2 is the quality of the filter and the sample after extraction.⁸

The molecular weight and distribution of molecular weight were measured with GPC on an Agilent 1100 column using polystyrene standards as the calibration.

RESULTS AND DISCUSSION

Variety of chromatic aberration and ultraviolet absorption spectrum

The samples of two polymers latex films of polyacrylate and poly(vinyl acetate-acrylate) were placed under the UV lamps for light irradiation aging and,

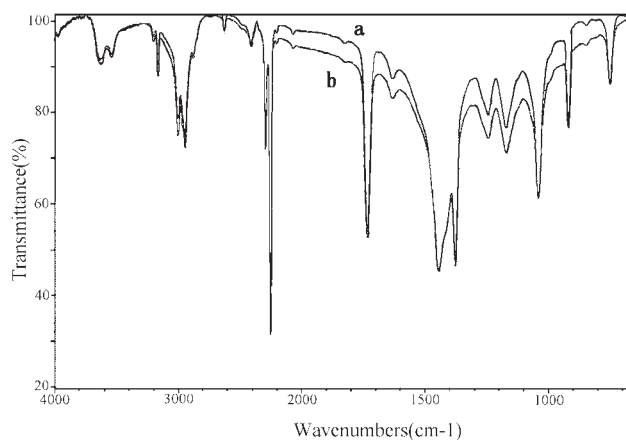


Figure 5 IR of poly(vinyl acetate-acrylate) before (a) and after (b) irradiation.

TABLE I
Content of the Characteristic Absorption peaks

Samples/groups rate	C _{C=O} ^a /C _{C=O} ^b	C _{C=C} ^a /C _{C=C} ^b
Polyacrylate	0.37	1.96
Poly(vinyl acetate-acrylate)	0.68	0.72

^a Represent before aging

^b Represent after aging.

as a result, the change of the color was shown in Figure 1.

Chromatic aberration was determined by a formula:⁹

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

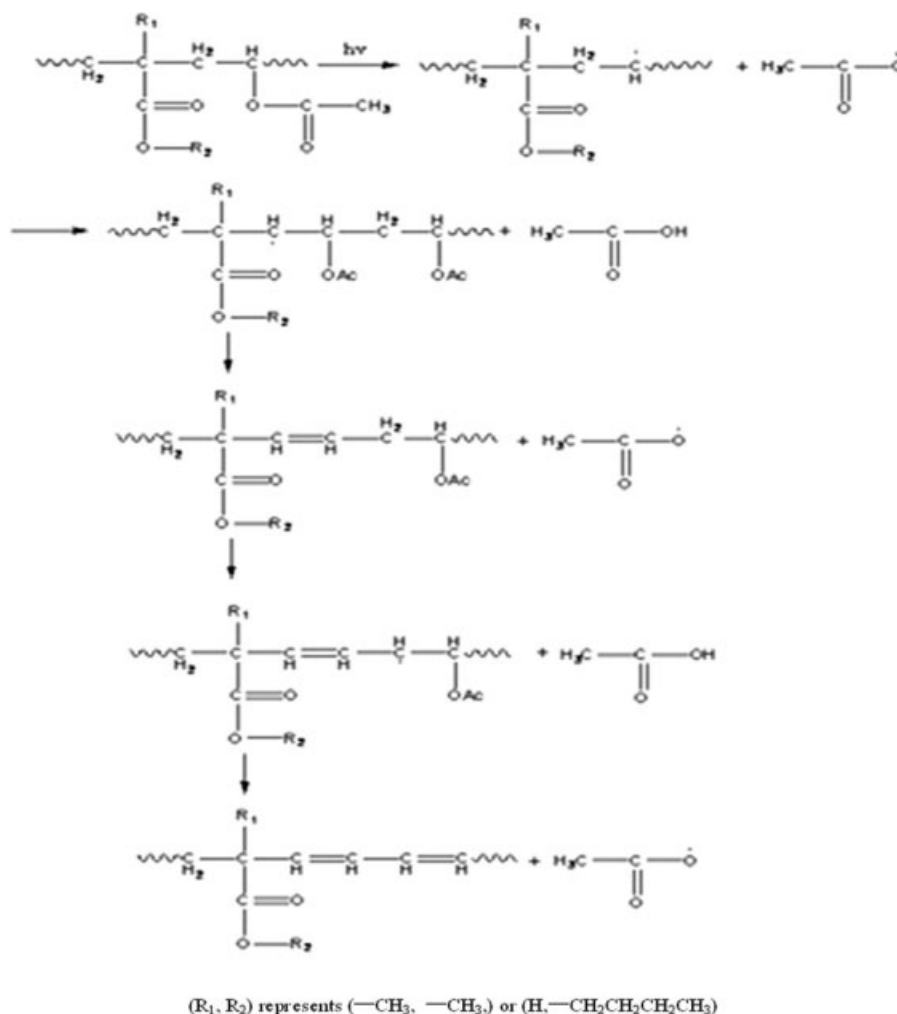
where ΔE is the chromatic aberration; ΔL^* is the lightness difference; Δa^* is the red-green, Δb^* is the yellow-blue.

According to the National Bureau of Standards (NBS), $\Delta E = 1.00$ acts as a NBS color units. And the

relationships between ΔE value and the value of color feeling are as follows: from 0 to 0.5 NBS units, the value of color feeling has a traces change and from 0.5 to 1.5, a minor change. From 1.5 to 3.0, a change can be aware of, while from 3.0 to 6.0, a change is identifiable and from 6.0 to 12.0, an obvious change can be found.

From Figure 1, alteration of ΔE of films of poly(vinyl acetate-acrylate) and polyacrylate, it shows that ΔE exhibits rising trend with the increase of aging time. Particularly in the curve of the poly(vinyl acetate-acrylate), there is the largest increase after irradiation of 240 h when ΔE has reached an identifiable color change grades, while the acrylate copolymer is correspondingly weaker.

Figures 2 and 3 are the ultraviolet absorption spectrums of polyacrylate and poly (vinyl acetate-acrylate), respectively. Taking the maximum absorption peaks at the wavelength of 246 nm in absorption spectrums as consideration, there is a little change in the peak area of polyacrylate before and after aging in Figure 2. Whereas the peak area of poly (vinyl



Scheme 1 Process of double bonds formation in poly(vinyl acetate-acrylate).

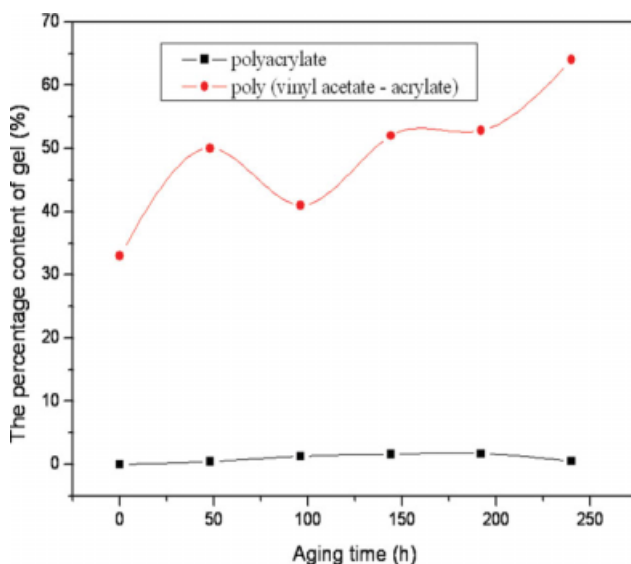


Figure 6 Changes of the percentage content of gel along with the aging time.

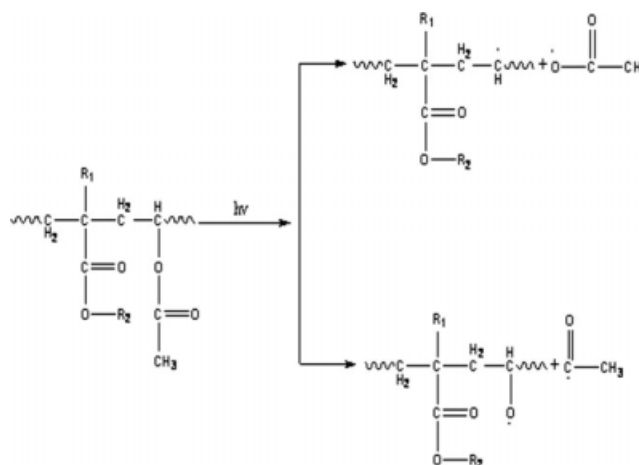
acetate-acrylate) evidently increases after aging as shown in Figure 3.

From the changes of the color and the results of the ultraviolet absorption spectra, it can be speculated that chromophore groups cause the deepening of the color. Since chromophore groups are unsaturated groups, in the process of UV irradiation, the double bonds, such as C=C and conjugated double bonds systems most likely generated in the films of polyacrylate and poly(vinyl acetate-acrylate). The result is in agreement with the research of McNeill IC, which said that yellowing may be attributed to the formation of conjugated double bonds.¹⁰ Some other researches also pointed that the change of color may be attributed to the formation of conjugated double bonds. When the number of conjugated double bonds reaches 4–5, the color will change into yellow. Based on this, it can be deduced that compared with polyacrylate, the film of poly(vinyl acetate-acrylate) is more prone to form chromophore groups under the UV irradiation.

Infrared absorption spectroscopy

In order to further understand the variety of chromatic aberration of the film of poly(vinyl acetate-acrylate) and polyacrylate, a contrasting research on the films before and after aging by infrared absorption spectroscopy was carried through.

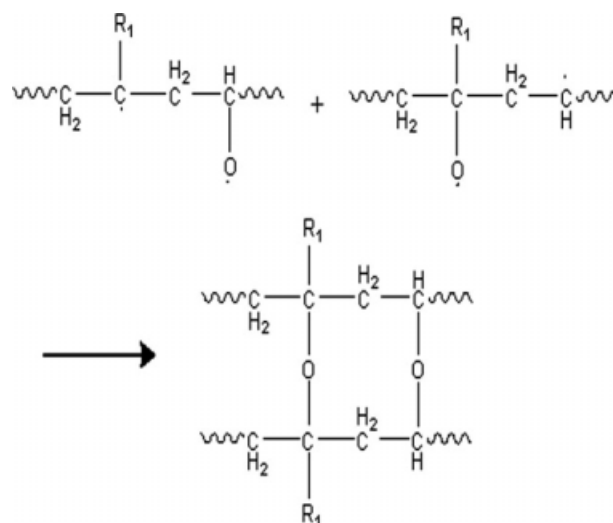
In Figures 4 and 5, the FTIR spectra show significant variation of after aging samples from before aging ones in the absorbance values of peaks at 1731 cm^{-1} , corresponding to carbonyl stretching, 1634 cm^{-1} corresponding to $>\text{C}=\text{C}<$ unsaturation and 1243 cm^{-1} for $-\text{COC}-$ antisymmetric stretching. In addition, 2252 cm^{-1} is corresponding to $\text{C}\equiv\text{N}$ stretching.



Scheme 2 Form of side chain scission in poly(vinyl acetate-acrylate).

Using the deformation of Lambert-Beer law, the content of characteristic groups before and after aging can be gained and listed in Table I.

It can be seen from the above results, in comparison to that of before aging, the content of carbonyl increases after aging and moreover the variety degree has some diversity to the two films. Therefore, it can be assumed that the reactions of carbonyl formation easily occur in polyacrylate and poly(vinyl acetate-acrylate) irradiation at 254 nm UV light. But, unexpectedly, the variety degree of polyacrylate is larger than that of poly(vinyl acetate-acrylate). Glikman et al.¹¹ pointed out that irradiation of polyacrylate in the presence of air produce radicals in the polymer chains which reacts with oxygen to give new carbonyl compounds. So, the results indicate that the existence of structural units of vinyl acetate in copolymer can restrain polyacrylate from reacting with oxygen. In



Scheme 3 Process of cross-linking reaction in poly(vinyl acetate-acrylate).

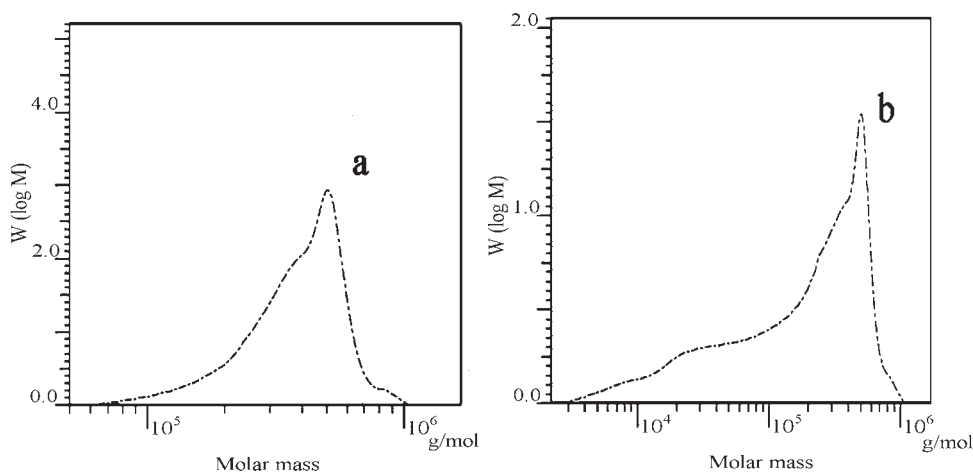


Figure 7 Gel permeation chromatography spectrums of polyacrylate before (a) and after 240 h aged (b).

addition, in poly(vinyl acetate-acrylate) the content of $>C=C<$ double bonds also markedly rises after the UV irradiation, which implies that double bonds were produced in poly(vinyl acetate-acrylate) and the color changes in aging procedure. It also can be speculated that the UV light may induce the formation of conjugated double bonds system.

From the above discussion, it is known that compared with polyacrylate, poly(vinyl acetate-acrylate) more easily forms double bonds. A process of double bonds formation in poly(vinyl acetate-acrylate) can be clearly presented as followed (Scheme 1).

Percentage of gel

It is well known that the formation of gel or cross-linking is another phenomena of aging, and simultaneously gel originates from double bond and free radicals. Therefore a research concerning gel should be deeply studied.

Here, the changes of the percentage content of gel along with the aging time are depicted in Figure 6. The changes of polyacrylate gel content with the aging time is slightly weak, illuminating that cross-linking reaction is correspondingly not obvious in the aging process. While in the film of poly(vinyl acetate-acrylate), the gel content with the aging time tends to strikingly rise. Before the aging the gel content of the original samples has reached 33% which probably because the film before aging was placed at room temperature for a long time. According to the phenomenon, it is easily conjectured that polyacrylate possesses more strong capability of resistant to aging than that of poly(vinyl acetate-acrylate). After aging for 240 h, the gel content rises to more than 60%, and it can be attributed to that cross-linking reaction of poly(vinyl acetate-acrylate) happens easily under UV irradiation. The increase of gel content is most likely derives from the side chain scission which can form free radicals, thereby initiating the cross-linking reaction. Therefore, from the curves

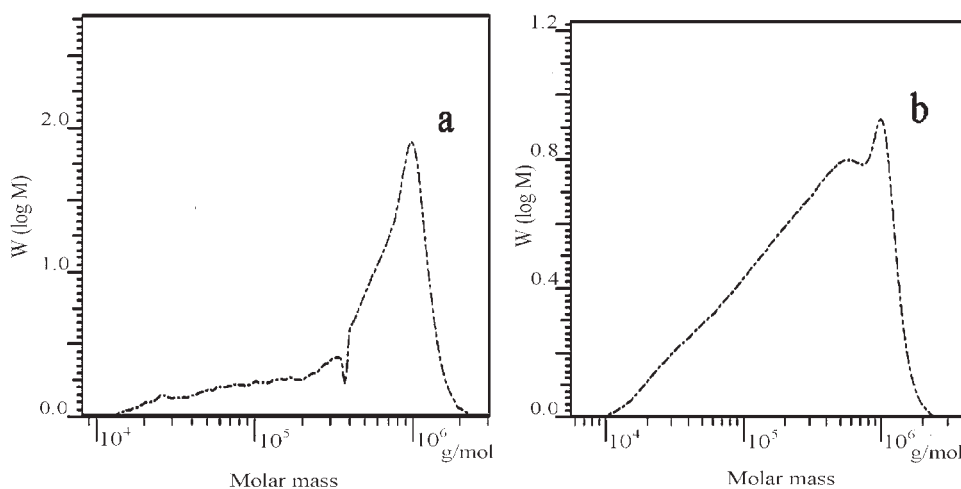


Figure 8 Gel permeation chromatography spectrums of poly (vinyl acetate-acrylate) before (a) and after 240 h aged (b).

TABLE II
Molecular Weight and the Molecular-Weight Distributions of Samples Before and After Aging

Samples	\overline{M}_n (g/mol)	\overline{M}_w (g/mol)	\overline{M}_z (g/mol)	\overline{M}_v (g/mol)	$\overline{M}_w/\overline{M}_n$
Polyacrylate (before aging)	3.2870×10^5	4.0439×10^5	4.6537×10^5	4.0439×10^5	1.2303
Polyacrylate (after aging)	5.6759×10^4	2.5986×10^5	4.2357×10^5	2.5986×10^5	4.5783
Poly(vinyl acetate-acrylate) (before aging)	2.0115×10^5	6.5963×10^5	9.3446×10^5	6.5963×10^5	3.2793
Poly(vinyl acetate-acrylate) (after aging)	1.3647×10^5	4.5505×10^5	8.0244×10^5	4.5505×10^5	3.3344

shown in Figure 6, it can be said that the introduction of vinyl acetate can aggravate side chain scission and consequently accelerate cross-linking reaction of poly(vinyl acetate-acrylate). Thus, a possible mechanism through which the reactions take place is shown in Schemes 2 and 3.

GPC

Besides cross-linking, do molecular weights of polymers have any change during the procedure? In order to prove the change, a relative study was done.

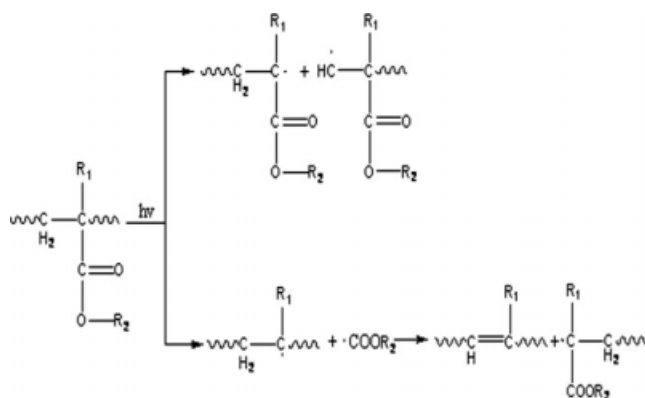
Figures 7 and 8 show the curves of GPC of polyacrylate and poly(vinyl acetate-acrylate) before and after aging. The changes of molecular weight and distribution of molecular weight are shown in Table II.

From the changes of the number average molecular weight and molecular weight distribution it can be seen that molecular weight of the two types of polymer all have a remarkably decline after aging, and furthermore molecular weight distributions are broadened. Changes of polyacrylate are larger whose molecular weight reduces to 17.3% of the original, and the width of molecular weight distribution has gone up to 3.72 times. However, molecular weight of poly(vinyl acetate-acrylate) drops to 67.8% of the original, molecular weight distribution width rises to 1.02 times. The results illuminate that main chain of polyacrylate and poly(vinyl acetate-acrylate) breaks seriously under UV irradiation, generating a large number of oligomers and small molecules. However

what is interesting is that the varieties of poly(vinyl acetate-acrylate) in molecular weight and molecular weight distribution are smaller than that of polyacrylate under UV irradiation, which suggests that the introduction of vinyl acetate inhibits the main chain from scission. According to the photo-degradation mechanism of polyacrylate (scheme 4),¹² it can be presumed that vinyl acetate is sensitive to 254 nm UV and easy to absorb UV light leading to the fracture of side chain and reducing the destruction of the light to the main chain. On the other hand, comparing with free radical of other vinyl polymer, the free radical of poly(vinyl acetate) has higher reactive activity, because of the weak conjugated effect between single electron of the free radical with acetyl. So, the free radical easily takes place chain transfer and generating branch chain, consequently inhibiting molecular weight from going down.

CONCLUSIONS

All the results from the study on accelerated aging polyacrylate and poly(vinyl acetate-acrylate) show that, under ultraviolet light radiation, the photodegradation reactions of poly(vinyl acetate-acrylate) also have three main procedures of the main chain scission, double bond formation, and the cross-linking reaction. However, the procedures all have more or less diversity from that of polyacrylate. Since poly(vinyl acetate-acrylate) more easily generates chromophore groups of double bonds or conjugated double bonds, the color of the film is deepened. With increase of the aging time, photodegradation of free radicals on side chains would be induced, finally causing the cross-linking reaction. Compared with poly(vinyl acetate-acrylate), polyacrylate has more seriously fracture on main chain, while the molecular weight remarkably reduced and distribution of molecular weight is evidently broadened, after being irradiated by ultraviolet light. Further research shows that the structural units of vinyl acetate introduced to polyacrylate can aggravate the formation of double bonds and result in the generation of cross-linking reaction. However, what is interesting is that the structural units can strikingly restrain main chain from scission. The results are



Scheme 4 Form of chain scission in polyacrylate.

possibly helpful for improving service life of polyacrylate coatings.

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