Surface Photografting Polymerization of Vinyl Acetate (VAc), Maleic Anhydride, and Their Charge Transfer Complex. II. VAc(2)

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ABSTRACT: On the basis of our earlier work, extensive experiments were conducted to further investigate grafting vinyl acetate onto different films (10 types of films and 20 kinds of film combinations), using various photoinitiators, for example, BP, AQ, ITX, XAN, Irgacure 651 and 184, acetone, and cyclohexanone, irradiated by UV radiation. Several means were applied to confirm the grafted PE-*g*-PVAc film. The results showed that increasing UV radiation intensity is favorable for grafting polymerization and the far UV radiation plays a decisive role. Among the photoinitiators tested, BP is the best one, because it was found that BP initiates the grafting copolymerization efficiently, and other initiators are less effective. To various combined substrates, the affinity between the monomer and films, the reactivity of hydrogens on the substrates, and the transparence of the top film to UV radiation are main factors affecting polymerization. Both direct method (FTIR) and indirect methods (contact angle, color reaction, absorption of dye and water) verified the true product PE-*g*-PVAc. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1522–1531, 2000

Key words: photografting polymerization; UV irradiation; vinyl acetate; benzophenone; film surface

INTRODUCTION

In the previous paper,[1] vinyl acetate (VAc) was successfully grafted onto low-density polyethylene (LDPE) films by UV irradiation with simultaneous method. Some important factors affecting the grafting polymerization were studied in detail. However, apart from these factors, that is, irradiation time, reaction temperature, oxygen (O_2), and the thickness of the monomer solution, the grafting polymerization may be related closely to other reaction conditions.

Various materials, for example, film,[2–4] plate or sheet,[5,6] fiber,[7,8] and bead[9] either different in composition, structure, or the degree of crystallinity and regularity, perform differently when used as substrate. Besides, it is necessary for the substrate to be transparent to some degree to the UV radiation.

In addition to the substrates mentioned above, the photoinitiator also deserves much attention. A number of different types of initiators have been used, for example, benzoyl peroxide (BPO),[10–12] azobisisobutyronitrile (AIBN),[13] benzoyldimethylketal (Irgacure 651),[14] benzophenone (BP),[11,12] biacetyl,[15,16] anthraquinone (AQ),[10–12] thioxanthone (TX),[17] and xanthone (XAN),[18] as seen in literature. On the other hand,

Table I   Thickness of Different Films

Film	Thickness (μm)
LDPE (thick)	114
LDPE (thin)	63
HDPE	16
PVC	152
OPP (thick)	39
OPP (thin)	19
PC	58
NY	17
PP	31
PVDF	51
PET	101

photografting polymerization also was conducted successfully without initiators.[19,20]

In order to obtain more complete understanding of grafting VAc onto substrates, an additional series of experiments was conducted in our laboratory. This article is devoted to studies of the effects of other principle factors, including the substrates and photoinitiators on the grafting polymerization of VAc irradiated by UV radiation onto films. In the present study, different films were used as the substrates and the initiating efficiency of various photoinitiators (BP, ITX, AQ, 651, 184, XAN, acetone, and cyclohexanone) were compared. In addition, several methods were applied to confirm the product PE-*g*-PVAc, such as Fourier transform infrared (FTIR) spectroscopy, color reaction, contact angle, and dye absorption by the grafted PE-*g*-PVA films.

EXPERIMENTAL

Materials

Commercial films, including low-density polyethylene (LDPE), high-density polyethylene (HDPE), poly(vinylchloride) (PVC), polypropylene (PP), oriented PP (OPP), polycarbonate (PC), poly-(hexamethylene adipamide) (NY), poly(vinylidene fluoride) (PVDF), and poly(ethylene terephthalate) (PET), with different thickness (listed in Table I), were first cut into circular samples about 70 mm in diameter and then subjected to Soxhlet extraction using acetone (or ethanol) as solvent for 5 h to remove impurities and additives in advance.
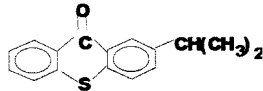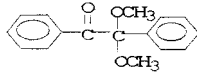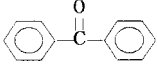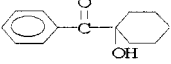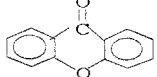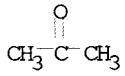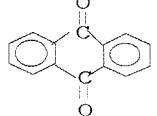
VAc was purified by distillation beforehand. BP was recrystallized from ethanol; others were

analytical grade, without further purification before use. All photoinitiators were dissolved in VAc in advance. The names and molecular structures of these photoinitiators are listed in Table II.

Grafting Polymerization Procedure

Photografting polymerization procedure was reported in detail in the preceding article. A certain amount of solution containing monomer and photoinitiator was deposited between the films with a microsyringe and pressed into a thin and even liquid layer. A piece of quartz plate was used to cover the films. The system was laid on the holder and irradiated with UV radiation (high-pressure mercury lamp, 1000 W). The polymerization degree was controlled by irradiation time. After po-

Table II   Photoinitiators

Photoinitiator	Molecular Formula
ITX	
651	
BP	
184	
XAN	
Cyclohexanone	
Acetone	
AQ	
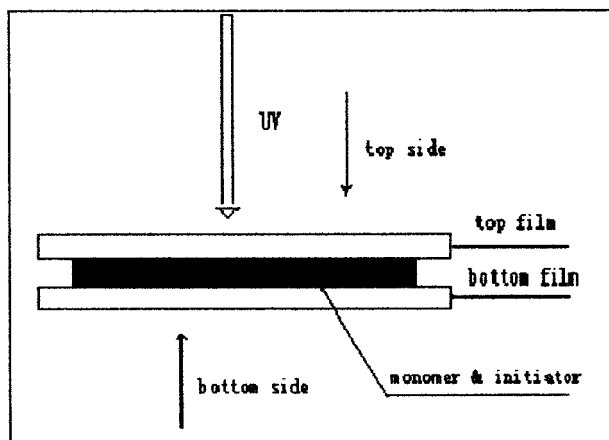
Figure 1 The assembly of the films for grafting polymerization.

lymerization, the films were taken out, separated, dried to constant weight, and then Soxhlet-extracted with acetone for 10 h to exclude homopolymer. The assembly of the films is illustrated in Figure 1.

Percent conversion (CP), percent grafting (GP), and grafting efficiency (GE) were defined according to the following formulas:

$$CP = \frac{W_P}{W_O} \times 100\% \tag{1}$$

$$GP = \frac{W_G}{W_F} \times 100\% \tag{2}$$

$$GE = \frac{W_G}{W_P} \times 100\% \tag{3}$$

where W_O is the weight of monomer between the two films; W_P is the weight of polymer formed, including homopolymer and graft polymer, which was obtained by weighing the films after vaporizing the residual monomer; W_F is the weight of the two films before polymerization; and W_G is the weight of the grafted polymer, which was obtained after extracting the homopolymer with acetone.

Alcoholysis

After VAc had been grafted onto a piece of PE film, the PE-g-PVAc film was formed. The grafted film with PVAc chains was dipped into the methanol solution containing NaOH and was kept at 30°C for about 1 h. After that, the temperature was elevated

to 45°C for another 1 h. Then, the film was taken out, washed, and dried to constant weight.

Characterization

FTIR Spectroscopy

A Fourier transform infrared spectrometer (50 DXC FTIR spectrometer; Nicolet, Northvale, NJ) was used to measure the IR spectrum of the grafted film sample PE-g-PVAc. Pure PE film was also measured as reference sample under the same conditions.

Contact Angle

The grafted LDPE film was first converted into PE-g-PVA film through alcoholysis. The contact angle of PE-g-PVA film against water was measured as follows. A piece of film (2×1 cm) was laid on the sample holder of the instrument of measuring contact angle. About 10 μL water was deposited on the film with a microsyringe. Then the instrument was adjusted until the contact angle was read clearly.

Color Reaction

By alcoholysis, PE-g-PVAc film was changed into PE-g-PVA film. That is, –OH groups were introduced onto PE-g-PVAc film, partly in place of –OCOCH$_3$ groups. The film sample was immersed in distilled water, in which a certain amount of iodine solution of ethanol (1%) was added. Several minutes later, the film exhibited color reaction.

Absorption of Dye

A certain amount of dye (cationic violet) was dissolved in water. A piece of PE-g-PVA film was put
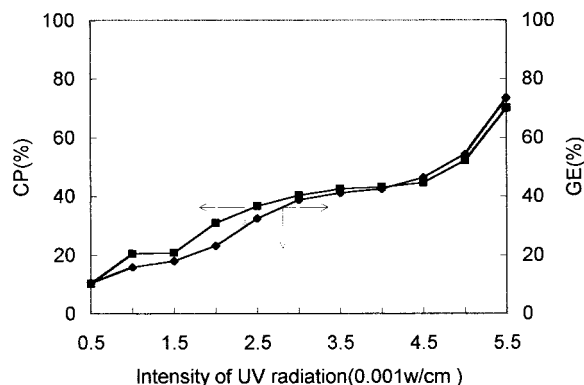
Figure 2 Effect of UV radiation intensity on polymerization. (■) CP; (♦) GE.
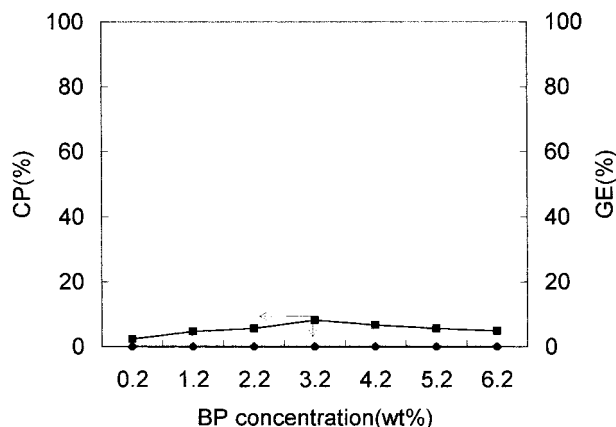
Figure 3 Effects of far UV radiation on polymerization. (■) CP; (♦) GE. Reaction temperature, 30°C; volume of VAc, 25 μL; reaction time, 8 min.

into it for a certain period of time. Then, the film was taken out and dried to constant weight. Dye absorption by the films was obtained via the following formula.

$$DA = \frac{W_{dye} - W_O}{W_O} \times 100\% \qquad (4)$$

where W_{dye} is the weight of dye absorbed by the film; and W_0 is the weight of film before absorbing dye.

RESULTS AND DISSCUSSION

Effects of UV Radiation Intensity on Polymerization

According to the literature, there have been no reports about the effects of UV radiation intensity

on photografting polymerization. Therefore, we conducted the relevant experiments, and the results are shown in Figure 2. OPP film was used to cover the substrates and lower the UV radiation intensity stepwise. The distance from UV lamp to the substrates was kept at about 15 cm.

It is observed from the curves in Figure 2 that along with the decrease of the UV radiation intensity, polymerization proceeds with more and more difficulty. That is, both curves of CP and GE tend to decline gradually. In Figure 2, when there is no OPP film used, the UV radiation intensity equalizes 5500 μW/cm² (λ = 254 nm), and when 10 pieces of OPP films were applied, it decreases to 1670 μW/cm²; when a piece of PET film is used to cover the film samples, it decreases sharply to 500 μW/cm², at which there is nearly no polymer generated. It is considered that PET film absorbs or screens the far UV radiation and works as a filter.[17] Yang and coworkers[13] thought that it is the far UV radiation (200–300 nm) that determines the polymerization. For the PE–VAc system, the effects of the far UV radiation on the reaction were examined, and the results are presented in Figure 3.

From Figure 3, it is observed that, though the reaction time is lengthened to 8 min (top side 4 min and bottom side 4 min), the grafting polymerization did not take place absolutely. Moreover, the homopolymer generated also was negligible. Accordingly, the far UV radiation determines the reaction during the photografting polymerization.

Effects of Photoinitiators on Polymerization

The behaviors of various photoinitiators in LDPE–VAc photografting polymerization systems have

Table III   Behaviors of Different Photoinitiators

Photoinitiator	Solubility in VAc[a]	Color of the Solution[b]	Polymerization[c]
Acetone	+	−	−
Cyclohexanone	+	−	−
AQ	−	Yellow	−
XAN	−	−	+
ITX	+	Light yellow	+
Irgacure 651	+	−	+
Irgacure 184	+	−	+
BP	+	−	+

[a] +, The photoinitiator dissolves with ease, and the concentration is 3 wt % of VAc; −, the photoinitiator dissolves with much difficulty, and the concentration is <1.5 wt % of VAc.
[b] −, Without color.
[c] +, Polymer formed; −, no polymer formed.
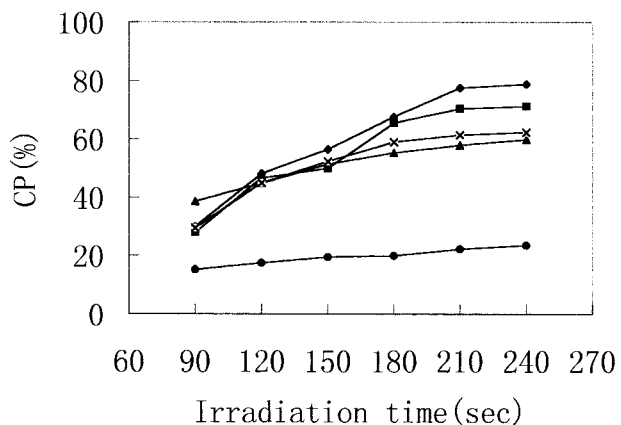
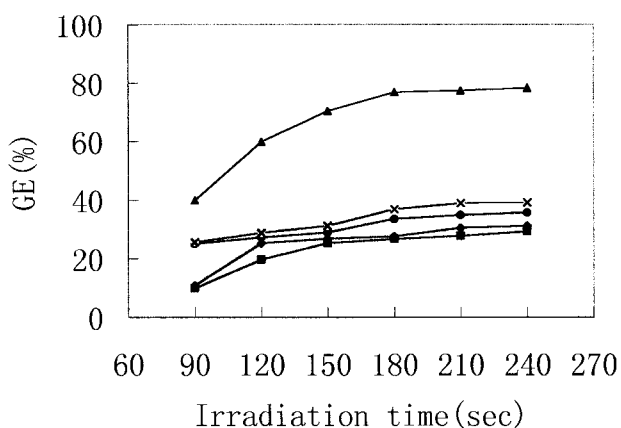**Figure 4** Effect of photoinitiators on polymerization. reaction temperature, 60°C; volume of VAc, 20 μL; UV intensity, 5010 μW/cm²; concentration of photoinitiators, see Table III. (A,B) (♦) 651; (■) 184; (▲) BP; (●) XAN; (×) ITX.

Regarding acetone and cyclohexanone, no polymerization took place. The reason may be that the concentration of acetone and cyclohexanone were too low (only 3 wt % of VAc). Elevating the concentration of them probably will bring about better results, which is under further examination.

To AQ and XAN, owing to that they do not dissolve in VAc smoothly, the concentrations of both of them were reduced to 1.5 wt % of VAc. Resulting from this, there was no polymer produced for VAc–AQ system and lower CP and GE for the VAc–XAN system.

Based on the above results, it is concluded that BP and ITX are more efficient than the other initiators in the investigation. Nevertheless, the product of PE-*g*-PVAc grafted film using ITX as the initiator seems to be light yellow. Among the

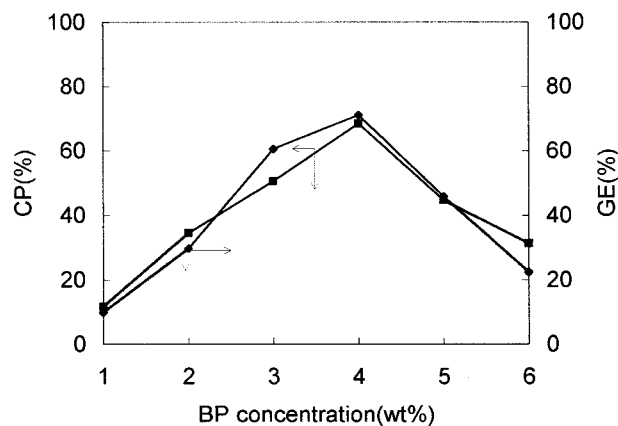been investigated. The results are indicated in Table III and Figure 4(A,B).

According to Figure 4(A,B) and Table III, acetone, cyclohexanone, and AQ cannot initiate polymerization of VAc, whereas 184, 651, XAN, ITX, and BP can be applied as the photoinitiators. From the curves of the CP, it is seen that 651 and 184 initiate more monomer to take part in reaction than BP does.

To 651 and 184, although more monomers undergo polymerization, maybe because of their high level of reactivity, much more homopolymer was formed than graft copolymer. Therefore, they are not fit to be used as initiators because too much homopolymer is generated and the GEs of these polymerization systems are too low.
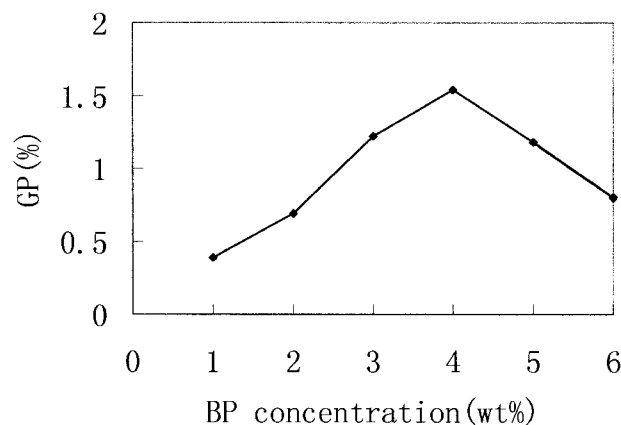

Figure 5 Effect of the concentration of BP on polymerization. Reaction temperature, 60°C; volume of VAc, 20 μL; UV intensity, 5400 μW/cm²; reaction time, 4 min. (A) (■) CP; (♦) GE; (B) (♦).

Table IV Behaviors of Different Film Combinations

$F_t//F_b$[a]	CP (%)	GE (%)	$W_{G,t}/W_{G,T}$ (%)[b]	$W_{G,b}/W_{G,T}$ (%)[c]
LDPE//LDPE[d]	60.8	74.6	75	25
LDPE//HDPE	34.9	56.9	97.3	2.7
HDPE//LDPE	24.1	36.4	20	80
LDPE//PC	48.8	68.5	100	/[e]
PC//LDPE	/	/	/	/
LDPE//OPP(19)[f]	37.6	65.7	100	/
OPP(19)//LDPE	39.2	35.6	7.6	92.4
LDPE//NY	53.8	51	45.1	54.9
NY//LDPE	53.2	62.9	79.3	20.7
LDPE//OPP(39)	48.9	65.9	91	9
OPP(39)//LDPE	22	68.3	6.7	93.3
LDPE//LDPE(114)	57	44.3	59.6	40.4
LDPE(114)//LDPE	50.5	59.6	71.4	28.6
LDPE//PP	54.3	77.2	44.8	55.2
PP//LDPE	62.4	46.6	72.2	27.8
LDPE//PET	83.3	53.5	44.6	55.4
PET//LDPE	13.9	15.4	50	50
LDPE//PVDF	62.3	66.4	53.2	46.8
PVDF//LDPE	37.6	68.6	79.1	20.9
LDPE//PVC[g]	50.2	55.3	49.8	50.2
PVC//LDPE[g]	28.9	51.2	62.5	37.5

Concentration of BP, 3 wt% of Vac; volume of VAc, 25 μL; reaction time, 4 min; reaction temperature, 60°C; UV intensity, 5010 μW/cm^2.

[a] The film combination: top film//bottom film.
[b] $W_{G,t}$, the weight of grafted polymer on the top film.
[c] $W_{G,b}$, the weight of grafted polymer on the bottom film; $W_{G,T}$, the weight of grafted polymer on two films ($W_{G,t} + W_{G,b}$).
[d] LDPE with thickness of 63 μm.
[e] The amount is too little to be weighed.
[f] The thickness of the films.
[g] PVC films were soften violently and the results were calculated approximately.

examined photoinitiators, BP is thus the most suitable. Moreover, the effect of the concentration of BP on the grafting polymerization was followed further, and the results are shown in Figure 5(A,B).

From the curves in Figure 5, it is suggested that the increase of BP concentration is desirable for the grafting polymerization, but when it exceeds 4 wt % of VAc, the effect is negative, that is, both CP and GE decrease markedly. Especially when the concentration of BP surpasses 6 wt % of VAc, only 27% and 7% of the monomer undergo polymerization and grafting copolymerization, respectively.

There are probably two reasons for this phenomenon. First, if too much BP is used and irradiated by UV radiation, a large number of macroradicals and semibenzopinakol free radicals are produced. Because of their much denser concentration, the probability of meeting and terminat-

Table V Transparence of Films to UV Radiation

	λ_1 = 254 nm		λ_2 = 297 nm	
Film	I_1	I_1/I_{10} (%)	I_2	I_2/I_{20} (%)
PVC	40	0.74	23	0.80
OPP(39)[a]	50	0.92	30	1.05
PET	50	0.92	30	1.05
PC	110	2.03	60	2.10
PVDF	2020	37.3	1200	42.0
LDPE(114)	2550	47.0	1420	49.6
NY	3200	59.0	1950	68.2
HDPE	3700	68.3	2100	73.4
LDPE(63)	3970	73.2	2230	78.0
PP	4290	79.2	2350	82.2
OPP(19)[a]	4540	83.8	2540	88.8

[a] The thickness of the film (nm); I_{10} and I_{20}, the intensity of UV radiation before penetrating film (I_{10} = 5420 μW/cm^2; I_{20} = 2860 μW/cm^2); I_1 and I_2, the intensity of UV radiation after penetrating films; λ_1 and λ_2, wave length of the UV light.

ing between them increases, resulting in less radical initiating polymerization. Second, when the amount of BP is elevated, the great part of UV radiation is absorbed and screened by the BP located at the top interface (illustrated in Fig. 9 in the preceding article[1]), leading to little UV radiation reaching the bottom interface. Therefore, the total amount of BP taking part in photoreduction decreases, initiating a small part of VAc to precede***** polymerization. Nevertheless, the second one is more plausible at present, because the formed semibenzopinalcol free radicals are too bulky, and they terminate with other radicals with much difficulty.

Effects of Different Substrates on Polymerization

The prerequisite for grafting VAc onto substrates effectively is to produce surface-free radicals by photoreduction between BP and the substrates. Here a variety of substrates have been examined, and the results are presented in Table IV.

There are together 11 kinds of films and 20 kinds of film combinations tested. According to Table IV, the behaviors of the films can be divided into three groups: polymerize smoothly [LDPE// LDPE, LDPE//PC, LDPE//NY, NY//LDPE, LDPE//OPP(39), LDPE//LDPE(114), LDPE(114)// LDPE, LDPE//PP, PP//LDPE, LDPE//PET, LDPE// PVC and LDPE//PVDF]; polymerize with difficulty [LDPE//HDPE, HDPE//LDPE, LDPE// OPP(19), OPP(19)//LDPE, OPP(39)//LDPE, PVC// LDPE and PVDF//LDPE]; and no polymerization took place (PC//LDPE).

In order to interpret the performance of these films, the affinity between VAc and the film, the reactivity of hydrogens in films, and the transparence of films to UV radiation should be considered carefully.

Affinity between Monomer and Substrate

In Ogiwara and coworkers'study,[21] acrylamide (AAm) was photografted onto PE films by means of two-step method. First, some monomers, for example, acrylic acid, methacrylic acid, acrylonitrile, and methyl methacrylate, were grafted onto films; then the grafted films were subjected to the second step, photografting with AAm. It was found that the affinity affects the surface photografting polymerization of AAm greatly.

In general, the better the affinity, the easier for the substrates to be wetted. A high level of affinity is thus favorable for the monomer to penetrate into the substrate. For surface modification, it is not desirable for the grafting polymerization to occur under the outermost layer and even into the deeper inner layer. For example, for PE and NY films, VAc is a kind of polar monomer to some degree, and the film of NY is more polar than that of PE. Thus, VAc diffuses more rapidly through NY film than it does through PE film.

Reactivity of Hydrogens in the Films

For the photografting polymerization system using BP as the photoinitiator, the reactivity of hydrogens in the substrates is one of the determinative factors influencing the polymerization. The reactivity of hydrogens is determined by two elements.

First, the degree of crystallinity and regularity of the substrate affects it directly. For a substrate with a high level of crystallinity, it is difficult for its atoms to leave their positions. Therefore, the mobility of hydrogens is restricted greatly. For example, the regularity and the crystallinity degree of HDPE are higher than those of LDPE. Consequently, it is more difficult for VAc to be grafted onto HDPE film. OPP is another convincing example. Compared with PP, the degree of orientation of molecule chains is much higher than that of PP. As a result, the $W_{G,b}/W_{G,T}$ of OPP//LDPE (6.7%) is much lower than that of PP//LDPE (72.2%).

Second, the structure of the substrate has great influence on the reactivity of hydrogens. The reactivity of hydrogens is shown as follows in the sequence of decline, NY > PET > PP > LDPE > OPP > PC.[22] The $W_{G,b}/W_{G,T}$ of these combined films decreases nearly in the same order. Of course, the influence of other factors has certain effects, making the sequence a deviation to some extent. Thus, the sequence is, LDPE//PET (55.4%) > LDPE//PP (55.2%) > LDPE//NY (54.9%) > LDPE//LDPE (25%) > LDPE//HDPE (2.7%) > LDPE//OPP, LDPE//PC.
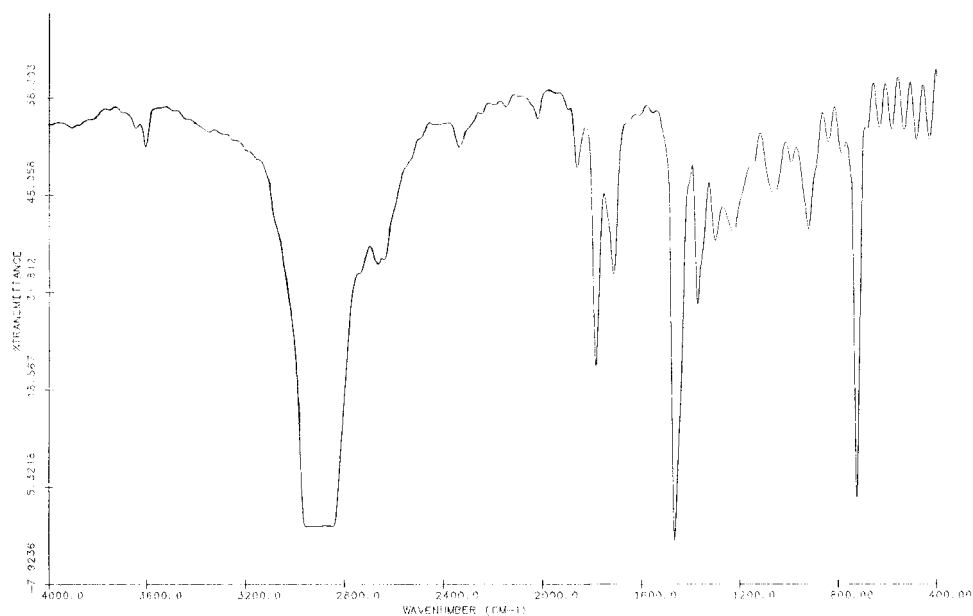
Transparence of Films to UV Radiation

In addition to the factors mentioned above, the transparency to UV radiation of different films also affects the polymerization. The transparency of the various films to UV light are examined and listed in Table V.

From Table IV, it is found that the same film samples, just differing in which one is placed on the top and which one is placed on the bottom, bring about different CP, GE, $W_{G,t}/W_{G,T}$ and $W_{G,b}/W_{G,T}$. Therefore, it is clear that there exists rela-
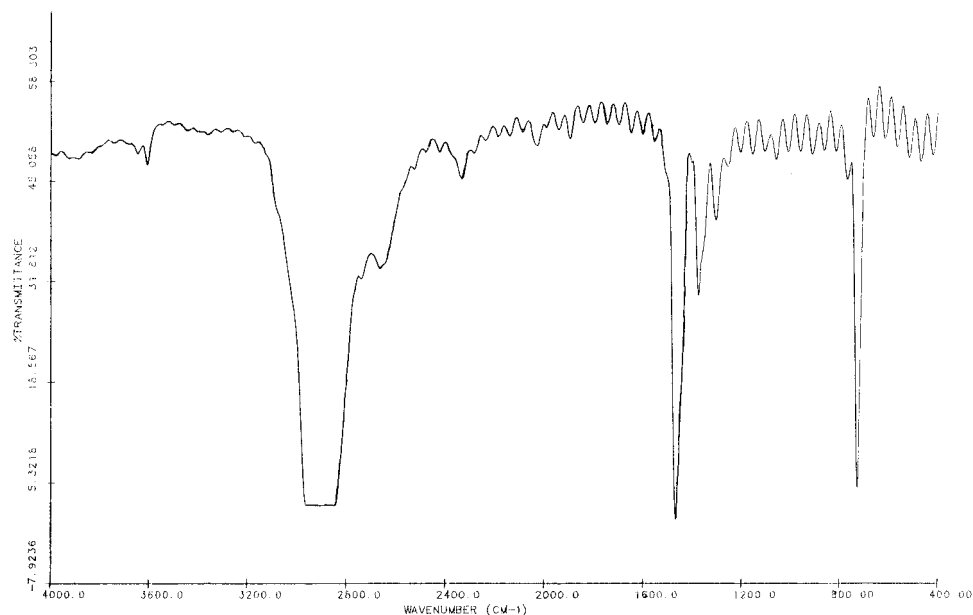
(a)

(b)

Figure 6   FTIR spectra of film samples. (A) PE film; (B) PE-*g*-PVAc film.

tionship between the grafting polymerization and the transparence of the films to UV radiation. Placing the more transparent film on top is more favorable to the polymerization.

Confirmation of PE-*g*-PVAc

FTIR Spectrum

After being Soxhlet-extracted for a long enough time (10 h) to remove homopolymer, the grafted samples (PE-*g*-PVAc) were tested with an FTIR spectrometer, together with the pure PE films. The IR spectra are shown in Figure 6.

Compared with the spectrum of pure PE film [Fig.6(A)], special vibration absorption bands in 1700–1800 cm^{-1} appeared in the IR spectrum of PE-*g*-PVAc film sample [Fig. 6B)]. The special vibration bands indicate the existence of carbonyl groups (–CO–). Because the homopolymer of VAc
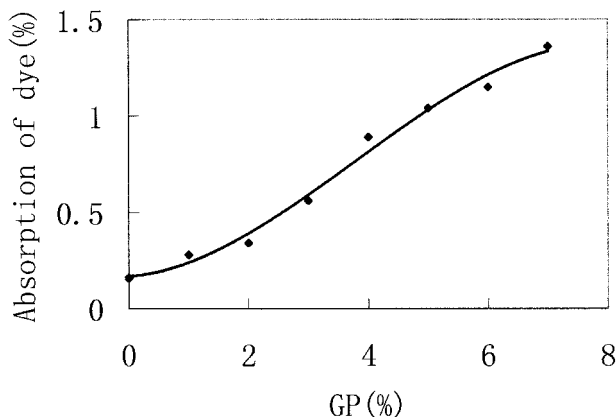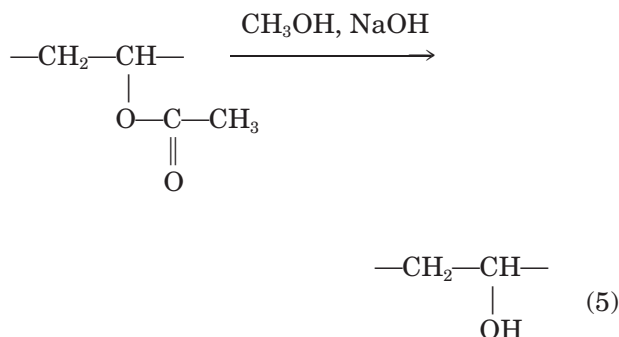
Figure 7 Absorption of PE-*g*-PVA film to dye.

had been removed absolutely, it is convincible to prove the sample to be PE-*g*-PVAc.

Color Reaction

Through alcoholysis, the –OCOCH$_3$ groups on the surface of PE-*g*-PVAc film could be turned into hydroxyl groups (reaction 5) and PE-*g*-PVA were produced.

$$\underset{\underset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\displaystyle O-C-CH_3}{|}}}}{-CH_2-CH-} \xrightarrow{\text{CH}_3\text{OH, NaOH}}$$

$$\underset{\underset{\displaystyle OH}{|}}{-CH_2-CH-} \quad (5)$$

PE-*g*-PVA films with or without residual –OCOCH$_3$ groups, deriving from parent PE-*g*-PVAc films, exhibit different colors incorporating with I$_2$. More detailed, PVA exhibits blue color when all –OCOCH$_3$ groups are changed into –OH groups and exhibit red color when residual –OCOCH$_3$ groups still exist.

In our studies, the PE-*g*-PVA exhibited red color because, in general, there is still some –OCOCH$_3$ groups left in PVA when PVA is obtained from the parent PVAc.[23] Nevertheless, it is safe to conclude that the graft copolymerization took place, and this color reaction method is convincing enough to be applied to verify the product PE-*g*-PVAc.

Dyeability

After alcoholysis, the film samples PE-*g*-PVA contain a great number of –OH functional groups. Immersed in the solution of cationic violet, they absorb dye gradually. The amount of dye absorbed is adequate to be examined by the gravimetric method. The results are described in Figure 7.

As illustrated in Figure 7, along with the increase of GP, the amount of dye absorbed by PE-*g*-PVA film also increased progressively. It is suggested that the produced PE-*g*-PVA samples showed better dyeability.

Wetability

Because of the hydrophilic property of hydroxyl groups, the wetablity of the PE-*g*-PVA films should be improved. Contact angles of PE-*g*-PVA samples against water are showed in Figure 8.

To monomer VAc, the GP is relatively less (<2% for grafting only once), because of the small amount of VAc used. However, as seen in Figure 8, the contact angles decrease markedly. The reason may be that the –OH groups are mainly located on the surface of the films, and VAc is an effective monomer used to modifying the surface properties of the polymeric materials.

In addition, the absorption of water by the grafted PE-*g*-PVA samples was examined too. Dipped in distilled water for a certain time, the samples were taken out, and the water covering the films was removed with filter paper. The measuring method was similar to that of measuring the absorption of dye. The results were shown in Figure 9. Although the amount of water absorbed
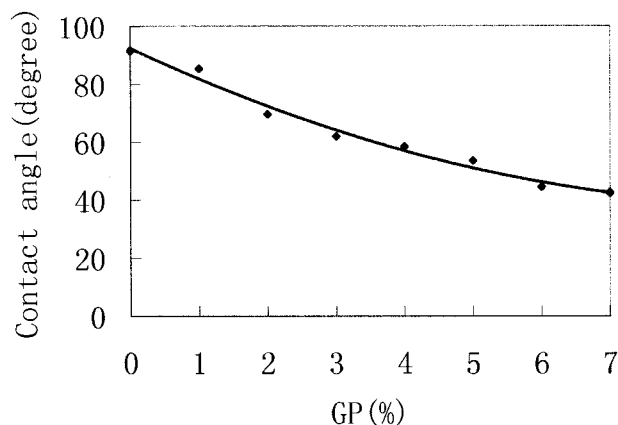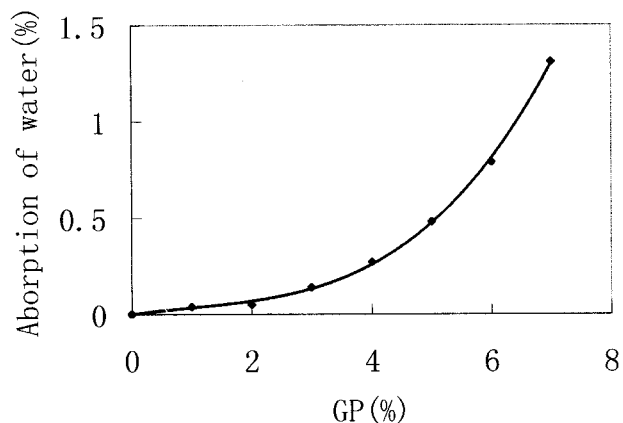

Figure 8 The relationship between contact angle and percent grafting.

Figure 9 Absorption of PE-*g*-PVA films to water.

was small, it is plenty enough to modify the surface wetability of the samples.

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