

Surface Photocrosslinking of Ethylene–Vinyl Acetate Copolymer Films

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ABSTRACT: Surface photocrosslinking of ethylene–vinyl acetate (EVAc) copolymer films containing benzophenone (BP) was investigated for the purpose of replacing a poly(vinyl chloride) floor. The photogelatin in the EVAc films was effectively observed after UV radiation in the presence of oxygen. The crosslinking reaction was initiated from the surface of the irradiated film, which was mainly due to the dehydrogenation and generation of macroradicals of polymer by the light absorption of BP. The experiments of polyethylene–VAc with BP showed that the VAc-rich amorphous part in the EVAc copolymer works as a crosslinking site. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1741–1745, 2000

Key words: ethylene–vinyl acetate; photoinitiator; benzophenone; surface crosslinking

INTRODUCTION

Nowadays, environmental problems have become one of the most important topics for material development. Poly(vinyl chloride) (PVC) products are considered to be harmful because of the generation of dioxin and hydrochloric acid after decomposition by fire. Therefore, non-PVC polymers are drawing more interest as substitutes for the PVC materials. For example, thermoplastic polyolefins have been widely investigated as recycling materials (material and thermal recycling) for flooring. However, the polyolefins have some thermal and mechanical shortcomings, such as lower dimensional stability and lower abrasion resistance. It is well known that crosslinking of the polymers is effective in improving these properties. Photo- and thermal crosslinking have been reported to especially modify surface and bulk mechanical properties for polyethylene (PE) and its copolymers.^{1,2} The photocrosslinking can be

controlled by UV light intensity and wavelength and the use of sensitizers or photoinitiators. However, photo- and thermal crosslinking of ethylene–vinyl acetate (EVAc) copolymers have been reported only for the PE derivatives. By adding crosslinking agent into the PEVAc the polymer chain can be crosslinked and degraded with the mechanism of dehydrogenation and deacidification.^{3–5} According to the thermal crosslinking of PEVAc with peroxides, the efficiency of crosslinking is very low compared to that of unsaturated polymers such as polybutadienes.⁶ Therefore, the photocrosslinking reaction of PEVAc can be controlled by surface irradiation of light and photosensitizers.

In this article we discuss photocrosslinking of crystalline EVAc copolymers in the presence of benzophenone (BP). It is known to be a good photoinitiator by UV irradiation and has good miscibility with EVAc copolymers. Generally, the photoreduction of the initiator with hydrogen abstraction, crosslinking, and oxidation of polymer macroradicals occurs only at temperatures above the glass transition temperature (T_g). When a photoinitiator like BP is added to the PEVAc, BP

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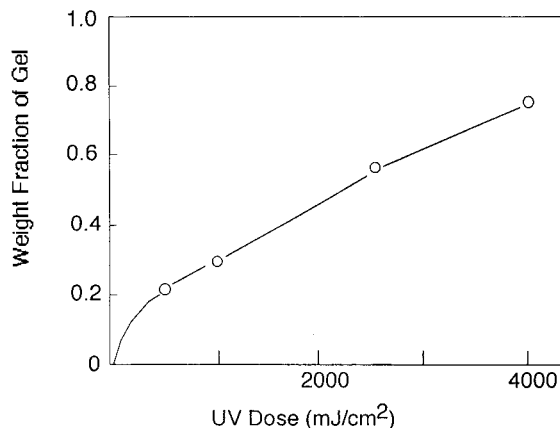


Figure 1 The relationship between the gel fraction and UV irradiation dose for a 20- μm thick film of PEVAc (75/25) containing BP (2.5 wt %).

absorbs the UV light which causes the breakdown and radical generation by which photocrosslinking of EVAc copolymer is initiated.

EXPERIMENTAL

The PEVAc (LV640, VAc content of 25%) was purchased from Mitsubishi Chemical Corp. The PVAc ($M_n = 5 \times 10^5$) was from JSR Corp. for a model experiment, and the BP was from Tokyo Kasei Co. Ltd. Polymer films were prepared by solution casting from a solution of tetrahydrofuran (THF) or toluene with the addition of different amounts of BP. The samples were kept under a vacuum after drying at room temperature. The film thickness was about 10–100 μm .

UV irradiation of the film samples was performed in N_2 , O_2 , or air at 65–70°C. The 80-W metal halide lamp light source was held at a 11.5-cm distance from the film samples. The gel fraction (W_{gel}/W_0) was calculated from the weight change after Soxhlet extraction for 8 h in THF or toluene. The glass transition temperature was measured by DSC (Rigaku 8230). The VAc content in the gel was obtained from TG measurements.^{6,7} The molecular weights by GPC and IR were determined with Tohso HLC801A and Perkin Elmer 6000 apparatuses, respectively.

RESULTS AND DISCUSSION

According to Loan's^{8,9} thermal crosslinking experiments of polymers with dicumyl peroxide, the

crosslinking efficiency of PEVAc is very low and forms soft materials with lower crosslinking density. The photoreaction is also assumed to give soft mechanical properties in pristine PEVAc that are due to the low crosslinking density.

Figure 1 shows the UV dose dependence of the gel fraction for a 20- μm film of PEVAc containing 2.5 wt % of BP. The gel starts from the lower dose and increases monotonously. The sample without BP has no gel in this UV dose range. The UV radiation may create free radicals or excited species from BP; the resulting BP-free radicals are capable of abstracting the hydrogen atom in the molecular chain of PEVAc, therefore initiating the crosslinking reactions. The higher the UV dose used, the more macroradicals formed, leading to an increase of the amount of crosslinking (i.e., the fraction of the gel with increasing UV dose).

Figure 2 shows the thickness dependence of the gel fraction for PEVAc (2.5 wt %) at a constant UV dose (4000 mJ/cm^2). We found that the gel fraction decreases with increasing film thickness. This implies that this photocrosslinking proceeds from the surface, and the gel is limited to a certain thickness under a fixed UV dose, especially for the thick films. From Figure 2 it is estimated that the crosslinked thickness is about 20 μm for the PEVAc/BP mixtures containing 2.5 wt % BP under a 4000 mJ/cm^2 UV dose. This means for a thin film ($\leq 20 \mu\text{m}$) almost all PEVAc molecules formed gel by the crosslinking reaction at this condition, and only the surface part was crosslinked for the thick film. This behavior may be attributed to the dependence of the energy of

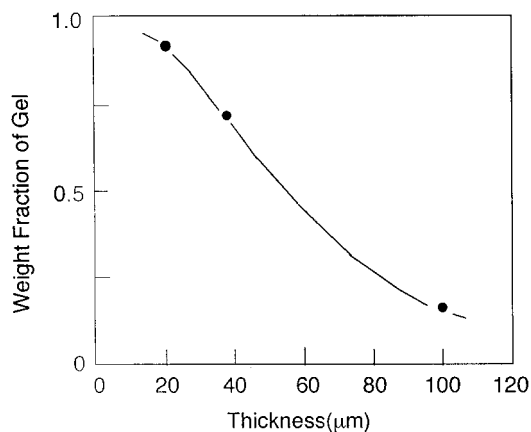


Figure 2 The relationship between the gel fraction and film thickness for PEVAc (75/25) containing BP (2.5 wt %) at a constant UV dose (4000 mJ/cm^2).

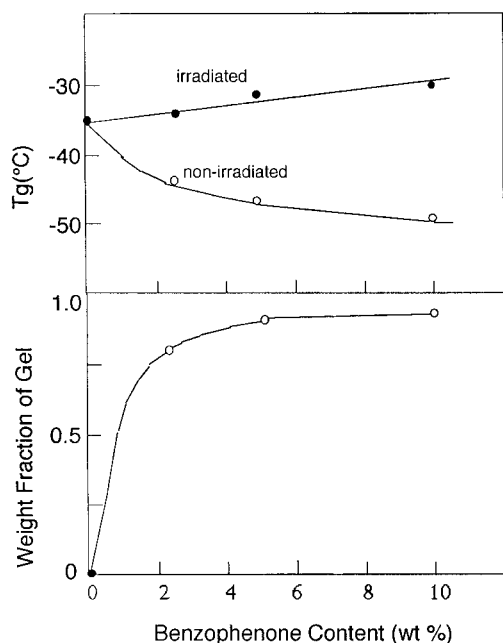


Figure 3 The change of the glass transition temperature T_g (from DSC) and gel fraction for PEVAc containing various concentrations of benzophenone.

the absorption light on the distance away from the film surface; in the surface region the absorbing energy is higher and thus more radicals are formed. Surface crosslinking should be dependent on film thickness, the light sources, and the light absorption characteristics of BP.

Figure 3 shows the relationship between the gel fraction and T_g for the samples with 20- μm thickness and containing different amounts of BP in air. The gel fraction appears with the lower concentration of BP and a lower dose and increases with increasing BP. No significant changes of T_g and IR spectra were observed in the samples after irradiation, suggesting the lower density of crosslinking sites.

The VAc content in the gel residue after the extraction of irradiated samples was about 30%, which is larger than the VAc content in PEVAc (25%). On the other hand, little change of crystallinity was observed from DSC curves after the irradiation. Considering that EVAc copolymer consists of VAc-rich amorphous regions and ethylene-rich crystalline regions, the increase of VAc content can only be explained by the fact that the crosslinking reaction occurred in the VAc-rich amorphous region. Because BP has good miscibility with VAc, it is probably concentrated in the sequence or terminal of polymer chains in the VAc-rich amorphous region and results in the

crosslinking reaction by formation of macroradicals.

Furthermore, we investigated the same photo-reaction in low or high density PE, and no gel was observed in this UV irradiation condition. Therefore, it can be concluded that the crosslinking reaction mainly occurs in the VAc-rich amorphous regions in PEVAc.

In order to verify the above conclusion further, it is necessary to investigate the photoreaction of the homopolymer of VAc. It is difficult to crosslink pure PVAc in the UV dose range used here,¹⁰ even though the crosslinking reaction of PVAc with BP easily occurs in air as shown in Figure 4. The glass transition temperature of PVAc increases with increasing BP after the irradiation. The gel fraction reaches 95%, a level similar to that in EVAc copolymers. This is evidence of a crosslinking reaction in the VAc-rich region of the EVAc copolymer. Little change of T_g is observed in the gel state after irradiation. This is probably due to the crosslinking reaction and chain scission, which was reported by Vaidergorin et al.³

Figure 5 shows X-ray diffraction patterns for the PEVAc film (20 μm) containing 5 wt % BP after UV radiation. The gel fraction of this sample is about 95%. The diffraction consists of three peaks from mainly ethylene sequence crystals

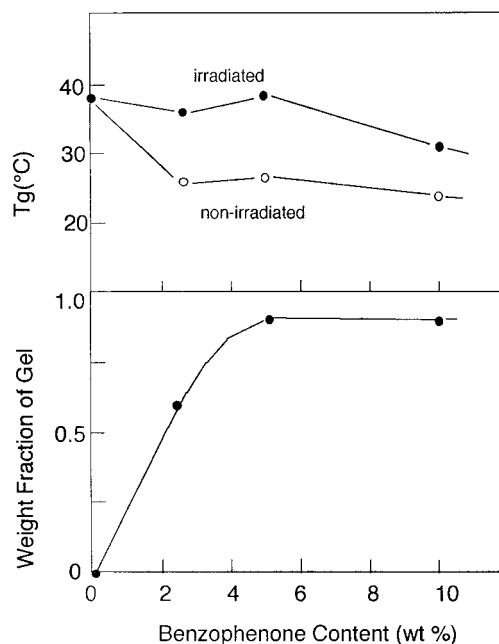


Figure 4 The change of the glass transition temperature T_g (from DSC) and gel fraction for homopolymer PVAc containing various concentrations of benzophenone.

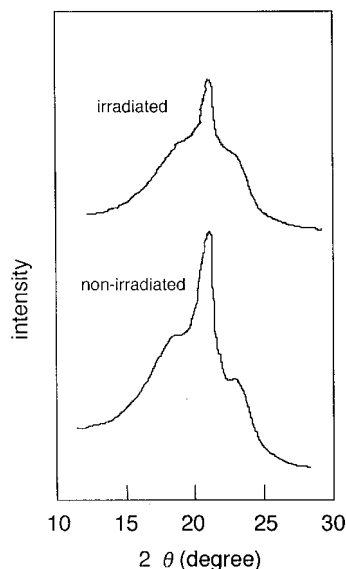


Figure 5 The X-ray diffraction pattern for PEVAc and the UV irradiated one.

and an amorphous halo from the VAc-rich sequence. After irradiation, the diffraction peaks become small because of the decrease in crystallinity after crosslinking. The crystals of the ethylene-rich sequence in PEVAc are easily disintegrated with photocrosslinking in the VAc-rich sequences.¹¹ This might induce the depression of the glass transition temperature. The schematic structure of photocrosslinked PEVAc is shown in Figure 6. Only the surface region ($\sim 20 \mu\text{m}$) is crosslinked by UV radiation for the PEVAc mixed with BP.

Figure 7 shows the relationship between BP concentration and molecular weight for the soluble part of irradiated PVAc in THF. The molecular weight of the soluble part decreases with the increase of PB, indicating scission of molecular

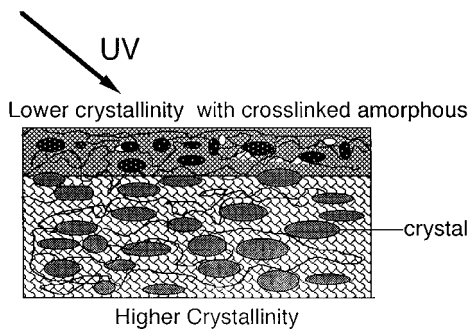


Figure 6 A schematic model of the structure for the UV irradiated PEVAc sample.

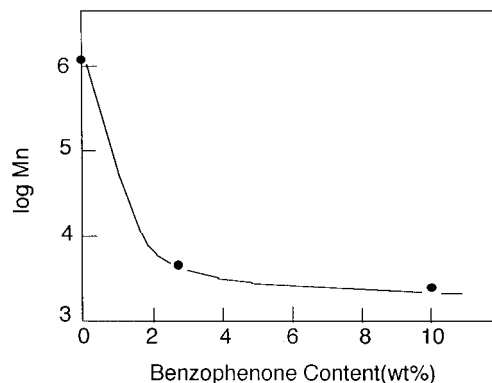


Figure 7 The relationship between the BP concentration and the number-average molecular weight (M_n) for the soluble part of irradiated PVAc in THF.

chains. Therefore, a higher dose of UV and a higher content of BP would induce photodestruction in PVAc. This behavior is similar to that of pure PVAc reported by Twing.¹⁰

Table I lists the gel fraction of samples irradiated in different atmospheres. The gel fraction of UV irradiated samples (viz. photocrosslinking efficiency) decreases in N_2 inert gas and increases in an O_2 or air atmosphere.

On the basis of spectroscopic data, if BP is used as the photocrosslinking initiator, the ketone part of BP in which the lowest triplet state has the (n, π^*) transition could be photoreduced in polymers to form radical pairs. If this radical pair disintegrates, the combination of macroradicals occurs and produces the crosslinks between the polymers. In such a case the ketyl radicals die from disproportionation or dimerization. However, in the presence of oxygen the reaction between oxy-

Table I Gel Fraction of PEVAc (PVAc)/Benzophenone (5%) Mixture Irradiated by Filtered UV

Samples	Gel Fraction (%) $\lambda >$	
	310 nm	220 nm
PEVAc in		
N_2	—	64
Air	—	95
PVAc in		
N_2	10	66
Air	51	82
O_2	56	—

UV irradiation was used at 4000 mJ/cm^2 .

gen and the polymer radicals possibly forms peroxy radicals. These in turn attack more polymer, form a hydroperoxide, and generate additional polymer-free radicals. The oxidation process may be accelerated by further decomposition of the hydroperoxide and may play the role of a catalyst for generation of radicals from the polymer.¹² So, in the presence of oxygen it is possible to increase crosslinking, but at the same time it may have a detrimental effect. In the case of PE the photocrosslinking reaction of PE with BP is reportedly more effective in essentially limited oxygen. Excess amount of oxygen mainly leads to the destruction of the polymer.

The crosslinking or destruction reactions proceed from the surface with both the diffusion of oxygen molecules and the photoreduction of BP. UV light should penetrate into the film samples with the disappearance of the absorption by photoreduction. Therefore, by controlling the conditions of the photoreaction we can get a crosslinked surface with good mechanical and adhesion properties with various adhesives.

In conclusion, surface crosslinked films of PEVAc can be gained by the addition of BP under UV irradiation. We can control the crosslinked

region (0–20 μm) by a lower UV irradiation dose. This photoreaction is very useful for the surface modification of films and fibers.

REFERENCES

1. Zamotaev, P. V. *Macromol Chem Macromol Symp* 1989, 28, 287.
2. Olayan, H. B.; Hamid, H. S.; Owen, E. D. *Rev Macromol Chem Phys* 1996, C36, 671.
3. Vaidergorin, E. Y. L.; Eunice, M.; Marcondes, R.; Toscano, V. G. *Polym Degrad Stabil* 1987, 18, 329.
4. Nakamura, S. *J Rubber Ind Jpn* 1970, 43, 753.
5. Sato, M.; Matsumura, M.; Emura, T. *J Rubber Ind Jpn* 1969, 42, 593.
6. Beveridge, C.; Sabiston, A. *Mater Design* 1987, 8, 688.
7. Chiu, J. *Appl Polym Symp* 1966, 2, 25.
8. Loan, L. D. *J Appl Polym Sci* 1963, 7, 2259.
9. Loan, L. D. *J Appl Polym Sci* 1964, 2, 3053.
10. Twing, G. H. *Discussion Faraday Soc* 1953, 14, 240.
11. Okui, T.; Kawai, T. *Macromol Chem* 1972, 154, 161.
12. Neff, W. E.; Frankel, E. N.; Weisleder, D. *Lipids* 1982, 17, 780.