Graft Polymerization of Acrylamide onto UV-Irradiated Films

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Synopsis

Graft polymerization of acrylamide was attempted onto the surface of films preirradiated with UV radiation. The films employed are nylon 6, polypropylene, and ethylene–vinyl acetate copolymers. Following UV irradiation in air on films without photosensitizer, they were placed in monomer solution, degassed, and then heated to 50°C to effect the graft polymerization. After rigorous removal of homopolymers, polyacrylamide chains were found to be grafted in the surface region of the films to amounts up to several hundred micrograms per square centimeter of films. An ESCA study revealed the UV-irradiated but not yet grafted surfaces to be oxidized, and formation of peroxides was strongly suggested by the reaction of irradiated films with 1,1-diphenyl-2-picrylhydrazyl. It is likely that the initiator responsible for the graft polymerization is peroxides generated at and near the film surfaces upon UV irradiation. The grafted films became very slippery when contacted with water, in contrast with the films UV-irradiated but not yet grafted.

INTRODUCTION

Surface properties of polymers are often as important as their bulk properties. Therefore, there have been reported a variety of surface modification methods, including acidic or alkaline treatment, corona or flame exposure, polymer deposit or coating, metal vapor deposit or ion plating, additive blending, and so on. Polymer grafting has been also employed for the surface modification or functionizing of polymers. The methods investigated for the surface grafting involve either immobilization of polymer chains onto a polymer surface by coupling reactions[1] or graft polymerization of monomers via glow discharge,[2,3] corona discharge,[4] and irradiation with ionizing[5] or UV radiation.

The use of UV irradiation seems to be an excellent method because of the simplicity and cleanness of its treatment. Until now, most of the photoinduced graft polymerizations have been carried out with a simultaneous irradiation technique in the presence of photosensitizers.[6,7] It is well known that UV irradiation results in a buildup of hydroperoxides for many polymers, regardless of the presence of photosensitizers, followed by polymer degradation.[8] Also in this work it will be shown that peroxides are introduced on the surface of polymer films upon UV irradiation. These peroxides may become an efficient initiator for surface grafting, similar to irradiation with high energy radiation[5] and plasma treatment.[3] To our knowledge, no work has been reported on graft polymerization of monomers onto polymer surfaces which have previously been irradiated with UV radiation in the absence of photo-

sensitizer. Recently Rånby and his co-workers have reported UV-initiated surface grafting of a vinyl monomer onto polymer surfaces,[9] but also their method is based on simultaneous irradiation of the substrate polymers in the presence of photoinitiators. The present work will describe the results of graft polymerization of acrylamide (AAm) onto films such as nylon 6, polypropylene (PP), and ethylene–vinyl acetate copolymer (EVA).

EXPERIMENTAL

Films and Monomer

Films of nylon 6, PP, Polyethylene (PE), EVA (VA content = 14, 19, and 28 mol %), and ethylene-vinyl alcohol copolymer (VAECO, ethylene content = 33 mol %) were of commercial grade, mostly having a thickness around 20 μm. Purification of these films were carried out by Soxhlet extraction with acetone or methanol for 24 h. AAm monomer, of gel electrophoresis grade, was purified by recrystallization from the aqueous solution.

Graft Polymerization

UV irradiation of films was performed with a high-pressure mercury lamp (75 W, Toshiba SHL-100UV type, $\lambda > 254$ nm) without any cutoff filter. Dried films were irradiated in air at ambient temperature by placing them 7 cm away from the center of the light source. Within 30 min after irradiation, graft polymerization onto the UV-irradiated films was carried out at 50°C with a deaerated aqueous solution of AAm at a concentration of 1.4M. The polymerization time was kept to 1 h, unless otherwise noted. To remove the homopolymer from the grafted films, they were first washed with running tap water and then immersed in a distilled water kept at 70°C overnight under continuous stirring. The amount of polyacrylamide (PAAm) grafted was determined by measuring the absorbance at 570 nm for the solution obtained after complete hydrolysis of the grafted PAAm with 1.5N HCl at 120°C and the subsequent reaction with ninhydrin.[2]

Surface Analysis

ESCA (XPS) spectra of UV-irradiated films were recorded with a Shimadzu ESCA-750 spectrometer using Mg-K$_\alpha$ excitation radiation.

The amount of peroxides generated on the film was determined by the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method. This method was intensively studied by Carley and Kitze with the help of tertiary diamine catalyst.[10] In the present work, thermal decomposition of peroxides and the subsequent reaction with DPPH was adopted instead of using the catalyst, as described earlier.[2] Briefly, the UV-irradiated films were placed in deaerated benzene containing 1.18×10^{-4} M of DPPH. After heating the benzene mixture at 70°C for 24 h, the optical density was measured at 520 nm (OD_{520}) on the benzene solution. The amount of peroxides per liter of DPPH solution was calculated from $\Delta OD_{520}/2 \times \varepsilon_{520}$, where ΔOD_{520} is a difference of OD_{520} between the starting and the irradiated film. ε_{520} of DPPH is 1.18×10^4 L mol^{-1} cm^{-1}.

Contact angle measurements were performed at 25°C with a sessile drop method.

RESULTS AND DISCUSSION

Surface Analysis of UV-Irradiated Films

ESCA spectra of the UV-irradiated nylon 6 films are shown in Figure 1, together with the unirradiated film. As is seen, N_{1s} and C_{1s} spectra do not exhibit a significant change upon UV irradiation, whereas O_{1s} spectra seem to have a new shoulder appearing at a high binding energy upon irradiation. This finding implies that oxygen atoms other than those in amide bond must be introduced on the surface of nylon 6 films. In Figure 2, differential O_{1s} core level spectra are shown, multiplying their intensity by a factor of 10. It is clearly seen that UV irradiation produces a new spectrum at a binding energy 1.5 eV higher than that of the starting film. This new spectrum probably corresponds to oxygen of peroxides formed upon UV irradiation.

The O_{1s}/C_{1s} intensity ratios calculated from the integrated area of spectrum for nylon 6 and other polymer films are plotted against UV-irradiation time in Figure 3. The O_{1s}/C_{1s} ratio increases in all cases with the irradiation time. For instance, the nylon film irradiated for 20 h has the O_{1s}/C_{1s} ratio higher than that of the unirradiated film by about 8%.
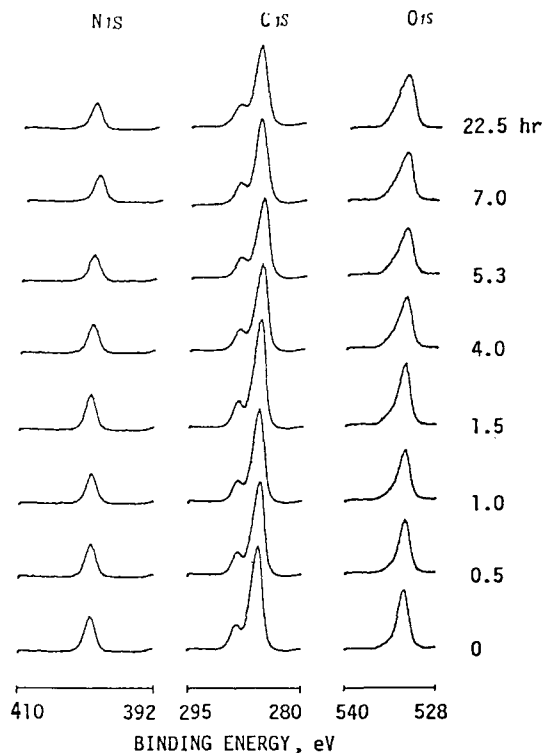

Fig. 1. N_{1s}, C_{1s}, and O_{1s} ESCA spectra of nylon 6 film untreated and exposed to UV radiation for different times.
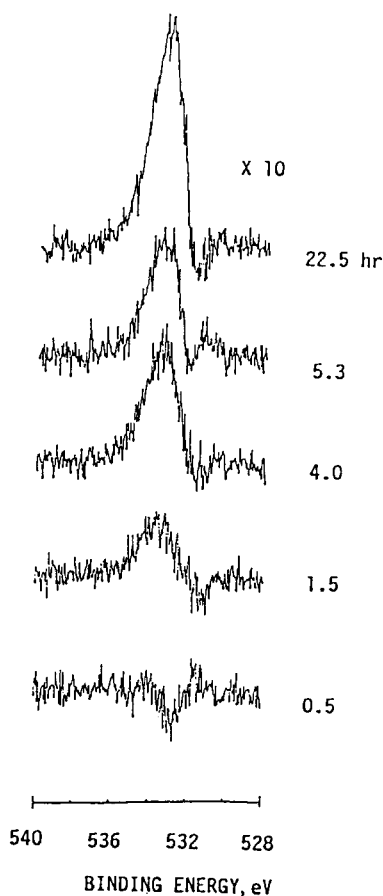
Fig. 2. Differential O_{1s} core level spectra for nylon 6 film exposed to UV radiation for different times.

The peroxide yields of UV irradiated films are shown in Figure 4, where it can be seen that peroxides are most markedly formed on the nylon and PP films by UV irradiation. The increase in peroxide concentration with the irradiation time is much larger than that of O_{1s}/C_{1s} ratio. This reason is not clear, but it seems that the different dependencies may be related to the difference in the depth below which the ESCA or DPPH method is no more applicable. It is likely that the nylon 6 film is oxidized to the depth much deeper than 50 Å from the surface, when UV irradiation is prolonged.

This tendency is more obvious for the PP film, as is seen in Figures 3 and 4. The increase in O_{1s}/C_{1s} ratio for the PP film irradiated for 20 h is only 0.3%, while the peroxide formed on the PP upon irradiation has a yield higher than that for the nylon 6 film. ESCA spectra of UV-irradiated PP films are shown in Figure 5.

UV light can probably penetrate through the PP polymer matrix more deeply than nylon 6, because a pure PP does not absorb any light of UV wavelength range. According to Carlsson and Wiles,[11] PP film undergoes photooxidation to 10^4 Å depth from the surface.
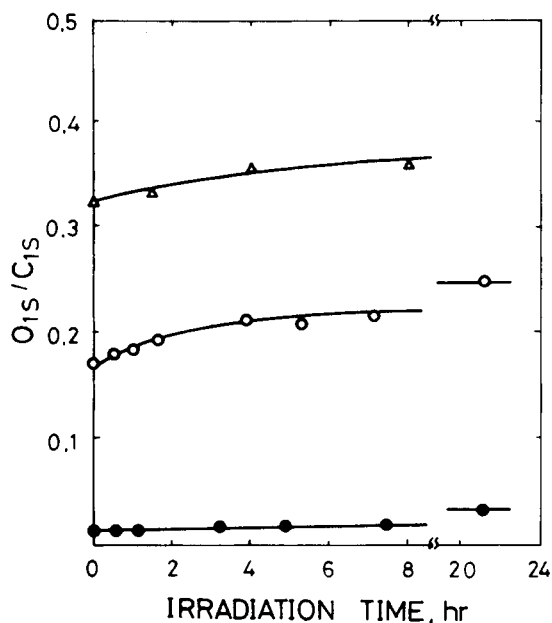
Fig. 3. Variation of O_{1s}/C_{1s} intensity ratio as a function of UV irradiation time: (○) nylon 6; (●) PP; (△) VAECO.

Expectedly, the UV-irradiated PP film became less wettable toward water than nylon 6 film. Changes of contact angle for several polymer films are plotted against the UV irradiation time in Figure 6. The contact angle is thought to be directly related to the properties of outermost surface layer of materials. The results in Figure 6 show the change of contact angles of
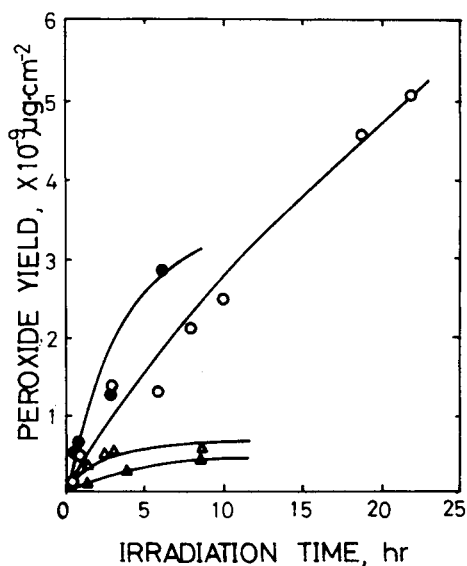

Fig. 4. Variation of peroxides yield as a function of UV irradiation time: (○) nylon 6; (●) PP; (△) PE; (▲) VAECO.
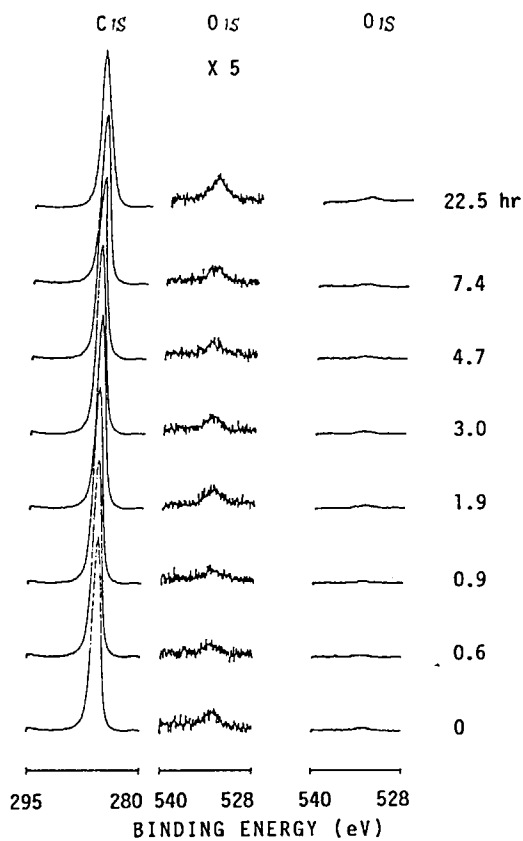
C 1s   O 1s   O 1s

X 5

22.5 hr

7.4

4.7

3.0

1.9

0.9

0.6

0

295   280 540   528   540   528
BINDING ENERGY (eV)

Fig. 5. C_{1s} and O_{1s} ESCA spectra of polypropylene film untreated and exposed to UV radiation for different times.
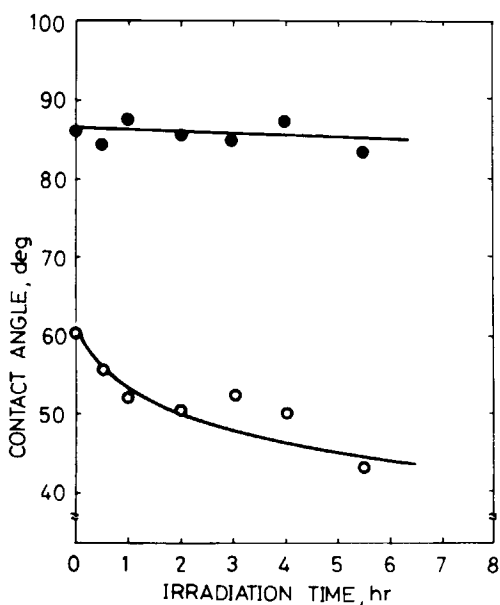
Fig. 6. Influence of UV irradiation time on the contact angle of films: (○) nylon 6; (●) PP.

UV-irradiated PP film to be much smaller than that for nylon 6 film, indicating that the hydrophilic groups such as peroxide group introduced on the surface of PP film is less than those for nylon 6.

Graft Polymerization onto UV-Irradiated PP and Nylon

The amount of PAAm grafted onto PP films was plotted against the preirradiation time in Figure 7. Graft polymerization takes place in high yields with the increasing UV preirradiation time, in accordance with the results of ESCA and DPPH measurement described earlier. It is likely that the graft polymerization was initiated by the radicals generated upon thermal decomposition of the peroxides formed at and near the film surface with UV irradiation in air. Light microscopic observation revealed that only a limited layer of cross section of PP film could be stained when the grafted PAAm was hydrolyzed to poly(acrylic acid) and then immersed in an aqueous solution of toluidine blue-O.

Graft polymerization of AAm altered the PP film surface from hydrophobic to hydrophilic and from nonlubricating to slippery surface. For instance, the contact angles of the PP films unirradiated and UV-irradiated for 5.5 h were 87° and 84°, respectively (see Fig. 6), whereas the film grafted to 120 μg cm^{-2} had a contact angle as low as 21°.

Graft polymerization of AAm onto the nylon 6 films preirradiated with UV took place as effectively as or more effectively than that for PP films. Unfortunately, amounts of PAAm grafted on nylon could not be determined with the ninhydrin method because of interference of amide bonds in nylon to the analysis. However, the nylon surface also became hydrophilic and slippery
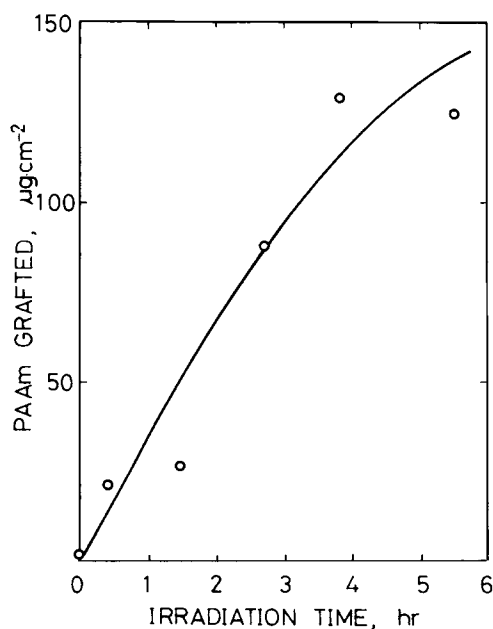

Fig. 7. Effect of UV irradiation time on graft polymerization of acrylamide onto polypropylene film.

TABLE I
Effect of UV Irradiation and Graft Polymerization of Acrylamide
on the Mechanical Properties of Films

| Film | Tensile strength (10^5 kg cm^{-2}) | | | | Elongation at break (%) | | | |
| | UV irradiation | | | | UV irradiation | | | |
	0 h	1.0 h	3.0 h	PAAm-grafted[a]	0 h	1.0 h	3.0 h	PAAm-grafted[a]
Nylon 6	6.1	5.70	5.81	5.79	392	422	404	435
PP	9.16	10.15	9.85	11.11	513	505	556	550

[a]AAm was grafted onto films preirradiated for 2.0 h.

by the graft polymerization. The contact angle of the nylon grafted with AAm after 5.5 h of UV exposure was 22°, whereas those of the starting and the irradiated film were 59° and 42°, respectively. Over the range of the exposure time studied, the UV irradiation had little effect both on the tensile strength and the elongation at break of the films as is shown in Table I. Also, SEM observation and IR measurement did not show any significant difference between the starting and the irradiated PP film. There have been published numerous works on photodeterioration or photooxidative degradation of polymer materials,[12,13] especially of PP. This polymer has been found to be very vulnerable to photodegradation because of tertiary carbon atoms present in the polymer chain. Therefore, much effort has been made to prevent PP from degradation or to stabilize PP against UV exposure. The surface grafting using UV preirradiation studied above is an application of the active species generated upon UV irradiation in the early stage where polymer chain does not suffer significant cleavage yet.

Grafting onto Other Polymer Films

EVA films having various vinyl acetate (VA) contents were used to attempt the surface grafting. The amount of PAAm grafted onto the preirradiated films was plotted against the preirradiation time in Figure 8. As is seen, graft polymerization takes place effectively also onto the EVA film irradiated with UV. The change of contact angle of the EVA film upon UV irradiation was small, independent of the VA content. For instance, the contact angles of unirradiated EVA films with VA contents of 14, 19, and 28% were 86°, 84°, and 85°, respectively, whereas those of UV-irradiated for 5 h were 81°, 79°, and 79°, respectively. However, the contact angle of the EVA films preirradiated for 4 h, followed by AAm grafting, became 10°–15°, irrespective of the VA content.

Figure 9 shows the dependence of the amount of PAAm grafted on the VA content of the EVA film. It is clearly seen that the EVA without VA component, that is, PE, is not grafted at all even under the prolonged irradiation (10 h), although a small amount of peroxides were detected as seen in Figure 4. The amount of PAAm grafted is not necessarily proportional to the amount of peroxides determined by the DPPH method. There are several factors influencing graft polymerization other than the peroxide yield. One of them is the permeability of monomer into the surface region of the irradiated
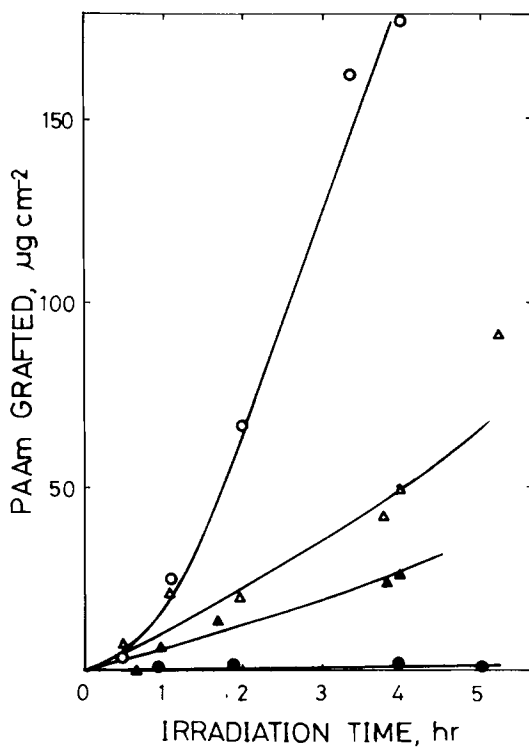
Fig. 8. Effect of UV irradiation time on graft polymerization of acrylamide onto polyethylene and ethylene–vinyl acetate copolymer films having various vinyl acetate contents: (●) VA 0% (PE); (○) VA 28%; (△) VA 19%; (▲) VA 14%.
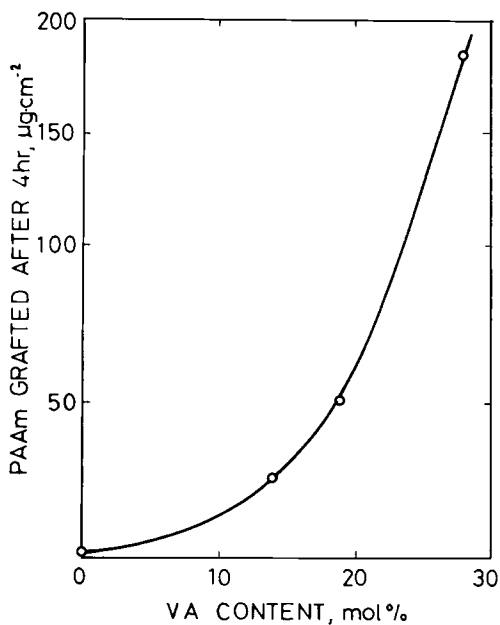

Fig. 9. Dependence of the vinyl acetate content on graft polymerization onto ethylene–vinyl acetate copolymer film preirradiated for 4 h.

polymer matrix. The monomer permeability depends not only on the glass transition temperature (T_g) of bulk polymer but on the hydrophilic property. In the case of VAECO film, which is relatively hydrophilic and has a low T_g, the PAAm grafted amounted to 452 μg cm^{-2} by preirradiation only for 1 h, whereas the amount of peroxides (Fig. 4) and the increase of O_{1s}/C_{1s} (Fig. 3) were not exceptionally large compared with those of other polymer films. Any significant graft polymerization of AAm did not take place onto UV-irradiated, hydrophobic films such as silicone and polytetrafluoroethylene.

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