Study of the Degradation of Polyurethanes. I. The Effect of Various Metal Acetylacetonates on the Photodegradation of Polyurethanes

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Synopsis

Photodegradation of polyurethanes based on polyester diol-diphenylmethane-p,p′-diisocyanate in the absence and presence of various metal acetylacetonates [Ti, V, Cr, Mn, Co(II), Co(III), Fe, Ni, Cu, Zn, Mg, Al, and Sn] was carried out; and the effect of these metal compounds on the degradation was examined by investigating the changes in the stress–strain properties and infrared- and ultraviolet-visible spectra of the polymer. The results obtained were as follows: Co(III), Co(II), Cu, Ti, and Sn acetylacetonates substantially enhanced the photo-oxidation of the polyurethane; and Al, Ni, and Zn acetylacetonates scarcely affected, or slightly retarded, it. The other metal acetylacetonates accelerated more or less the photo-oxidation of the polymer. Co(III), Co(II), and Cu acetylacetonates extremely degraded the polymer during the processing of the sample films as a result of the thermal degradation. Wavelength of the irradiated light was responsive to photochemical reactions of functional groups in the polymer. C—N and C—O bonds of urethane groups were very accessible to the photo-irradiation both without and with a glass filter, while methylene groups were rather stable to the irradiated light longer than 300 nm, through a glass filter. The effect of the metal compounds on the coloration of the polymer was also consistent with that of mechanical strength and infrared spectral changes.

INTRODUCTION

Since polyurethanes appeared as one of the new industrial materials,[1-4] the steady, substantial, world-wide growth in the manufacture and use of the urethane materials has been continued because of their high mechanical-performance properties.

It is well known that most polyurethanes are based on aromatic diisocyanates such as diphenylmethane-p,p′-diisocyanate and tolylene diisocyanates,[1,2] with amine compounds and metal compounds[1-13] being used as catalysts for the urethane-forming reaction. Polyurethane foam on an industrial scale is normally produced by a single-stage method in the presence of a catalyst mixture of tin diethyldicaprylate and triethylene diamine.[14]

The materials obtained, however, have increased sensitivity to hydrolysis, or thermal and photodegradation, which causes a marked deterioration of physical and mechanical properties, especially in the presence of a trace amount of metal compounds, whether from the residual catalyst or from contaminants occurred during the processing.[15] Extensive study has, therefore, been carried out on the degradation of the polyurethanes and model ure-

thanes with regard to protection and elucidation of the reaction mechanism, and also on the development of new diisocyanates that give highly stable polymers.[13–36] However, no systematic study seemed to be carried out on the effect of metal compounds on the photodegradation of polyurethanes.

We have been interested in the catalytic action of various metal compounds on the thermal and photodegradation of polymers and have clarified the effect of a series of transition metal stearates on the degradation of polyolefins.[37,38] Herein, we discuss the effect of various metal acetylacetonates on the photodegradation of polyurethane based on polyester diol-diphenylmethane-p,p′-diisocyanates, on the basis of the changes in stress–strain properties and infrared- and ultraviolet-visible absorption spectra of the polymer.

EXPERIMENTAL

Preparation of Test Sample

Diphenylmethane-p,p′-diisocyanate (210 part by weight; 0.84 mole) was reacted with a macroglycol, poly(tetramethylene adipate) glycol, MW circa 1000 (500 part by weight; 0.50 mole) at 80°C for 5 hr under a stream of nitrogen. After cooling to room temperature, the contents were dissolved in dry dimethyl formamide (432 part by weight) and methylethyl ketone (1296 part by weight). Then, 1,4-butanediol (28.5 part by weight; corresponding to NCO/OH molar ration 1.00/0.96) was added and reacted at 70°C for 8 hr under a nitrogen stream. n-Propyl alcohol (7.4 part by weight) was used to end the reaction. The polyurethane solution thus obtained was 30 wt-% of polyurethane component, and its viscosity was 76,000 cP at 25°C.

For the preparation of mechanical-property test films, a portion of the polyurethane solution was cast on a silicone-coated paper and dried in a desiccator *in vacuo* at ambient temperature for 1 hr. The cast films were kept in an oven at 80°C for 20 min, then cured at 120°C for 20 min (the temperature was raised at the rate of 20°C/min, which took 20 min). For the preparation of spectrometry films, a portion of the polyurethane solution was cast onto a silicone paper or a quartz plate and dried *in vacuo* at ambient temperature for 48 hr.

Photo-Irradiation

Test films were placed at right angles to, and at a 10-cm distance from, the light source, a Toshiba high-pressure mercury lamp (main wavelengths at 2537, 2900, and 3650 Å), and were irradiated without and through a glass filter at wavelengths longer than 3000 Å at ambient temperature for various times up to 50 hr.

Characterization of Sample

Characterization of samples was made by measurements of the changes in stress–strain properties and infrared- and ultraviolet-visible spectra of the polymers.

Stress–Strain Property

Stress–strain curves for each sample (micro dumbell) were recorded on a Tensilon (Toyo Seiki Co., Ltd.) upright dial gauge-type US-11, and tensile

strength and elongation at break were determined. Before testing, all samples were conditioned overnight at 50% relative humidity and 20°C; and five measurements were carried out for each sample, and the average values were calculated.

Infrared Spectrum

Infrared absorption spectrum of each film sample was recorded on a double-beam grating spectrometer, Hitachi EPI-G3. The changes in the spectrum at 1075, 1525, 1780, 2920, and 3400 cm^{-1} and other wavelengths were analyzed by a base-line method.

Ultraviolet-Visible Spectrum

Ultraviolet-visible absorption spectrum measurements were made with a Hitachi double-beam-type spectrometer, Hitachi 124-type.

RESULTS AND DISCUSSION

Mechanical Property

Stress–strain curves of representative samples are given in Figure 1.

As shown in Figure 1, the stress–strain curves for polyurethane alone show the modulus and high strength of a rubbery polymer after 10 hr of photo-irradiation. However, in the case of polyurethane containing Co(III) acetylacetonate, a large loss of mechanical strength is observed in the original sample. From the stress–strain curves of all the original samples, tensile strength and elongation at break were determined. The results obtained are summarized in Table I.

The results shown in Table I apparently indicate that the presence of Co(III), Co(II), and Cu acetylacetonates remarkably lowers the tensile
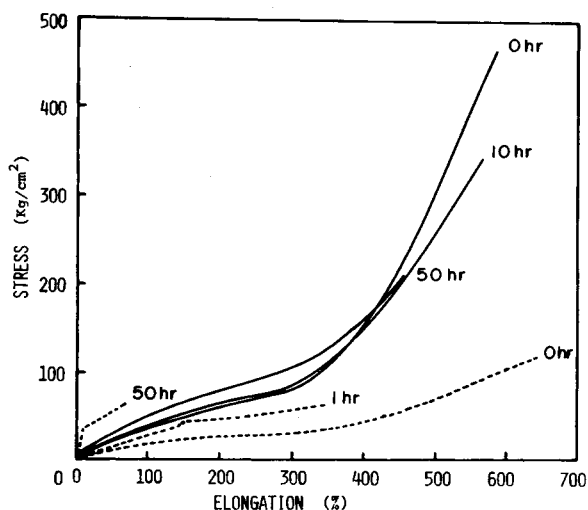

Fig. 1. Stress–strain curves of representative samples (without a glass filter 0.1 ± 0.01 mm) 20°C, 50% R.H.: —— = polyurethane alone; - - - - = polyurethane containing Co(III) acetylacetonate.

TABLE I
Tensile Strength and Elongation at Break of Original Samples

Additives	Tensile Strength Break,%[a]	Elongation Break,%[a]	Additives	Tensile Strength Break,%[a]	Elongation Break,%[a]
None[b]	100	100	Fe (III)	97	108
Mg (II)	97	106	Co (II)	59	109
Al (III)	117	101	Co (III)	28	110
Ti (IV)	80	107	Ni (II)	98	115
V (III)	97	99	Cu (II)	66	104
Cr (III)	91	100	Zn (II)	91	116
Mn (II)	95	108	Sn (IV)	101	107

[a] Relative percentage to None.

[b] None: 457 kg/cm^2; EB of None: 585%.

strength of the polyurethane, while none of the metal acetylacetonates examined lowers the elongation of the polymer. It implies that some metal acetylacetonates obviously affect the physical properties of the polymer during the curing process. The effect of heat treatment on the properties of the polymer will be described at the end of this paper.

The changes in tensile strength and elongation of representative samples during photo-irradiation are shown in Figures 2 and 3. From these figures it is clear that (1) the presence of metal acetylacetonates remarkably affects the photodegradation of polyurethane; (2) substantial decrease in mechanical strength of the polymer occurs at the initial stage of the photo-irradiation; and (3) after circa 25 hr of irradiation, less change is observed.

Schollenberger et al.[23] explained that the loss in tensile strength upon initial exposure of the polymer was probably the result of surface embrittlement
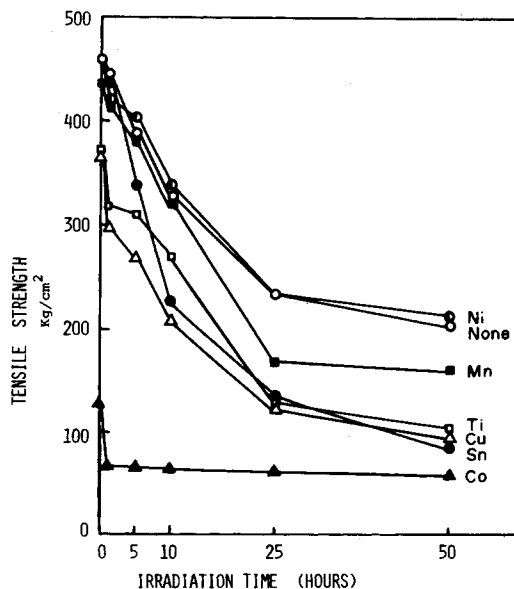

Fig. 2. Changes in tensile strength of representative samples after photo-irradiation (without a glass filter; 0.1 ± 0.01 mm).
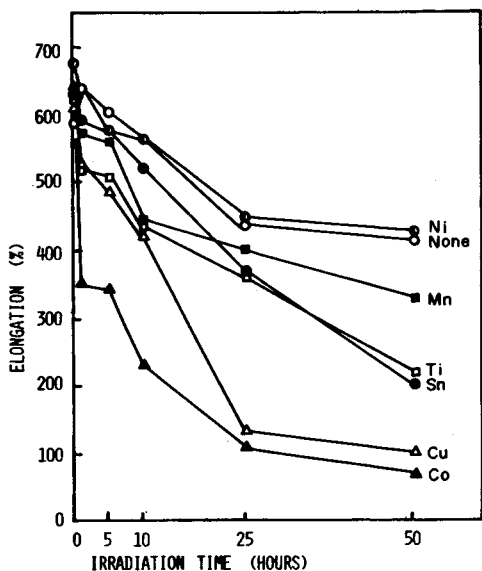
Fig. 3. Changes in elongation of representative samples after photo-irradiation. (without a glass filter; 0.1 ± 0.01 mm).

and that the failure of subsequent exposure to further reduce the strength properties was thought to result from the reduced air permeability of its continuous, tightly crosslinked surface. The same explanation can be applied to the results mentioned above.

The comparison of tensile strength and elongation of all original and 50-hr photo-irradiated samples is shown in Figures 4 and 5. As shown in Figures 4 and 5, Co(III), Co(II), Cu, Ti, and Sn acetylacetonates remarkably accelerate the photodegradation of polyurethane; but Al, Ni, and Zn acetylacetonates scarcely cause any effect. The other metal acetylacetonates accelerate more or less the photo-oxidation of the polymer.
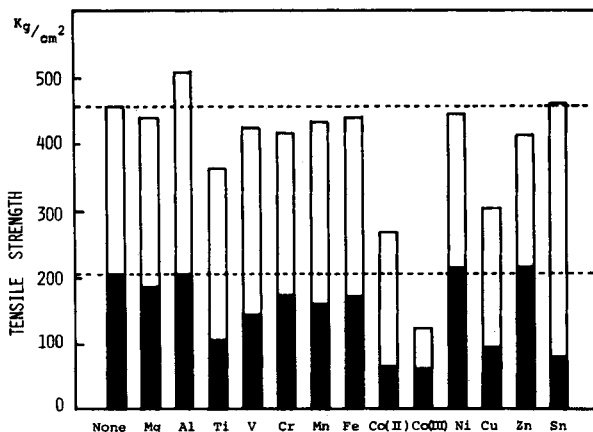

Fig. 4. Comparison of tensile strength of original and 50-hr photo-irradiated samples (without a glass filter; 0.1 ± 0.01 mm): □■ = original; ■ = 50-hr photo-irradiated.

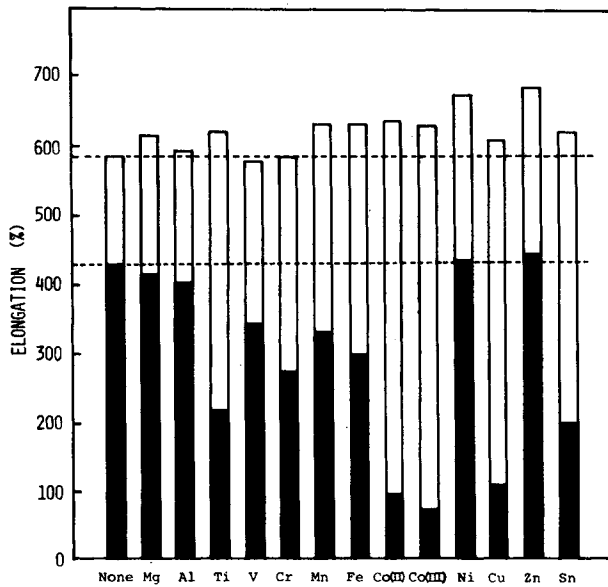Fig. 5. Comparison of elongation of original and 50-hr photo-irradiated samples (without a glass filter; 0.1 ± 0.01 mm): □■ = original; ■ = 50-hr photo-irradiated.

Infrared Absorption Spectrum

Schollenberger and Stewart[2] and Corish[22] gave comprehensive assignments of infrared absorption spectra of polyurethanes and explained the changes in the absorption spectrum during photo-irradiation of the polymer. They emphasized the decline of aromatic urethane structures and so on during the photo-irradiation.

As shown in Figures 6 and 7, similar changes in infrared absorption spectra are observed in the same spectral regions, and the presence of Sn acetylacetonate remarkably accelerates the changes in infrared absorption spectra of the polymers. Figures 6 and 7 also demonstrate that the changes in polyurethane structure during the photo-irradiation are very responsive to the wavelength of irradiated light. Namely, when the polymer is irradiated through a
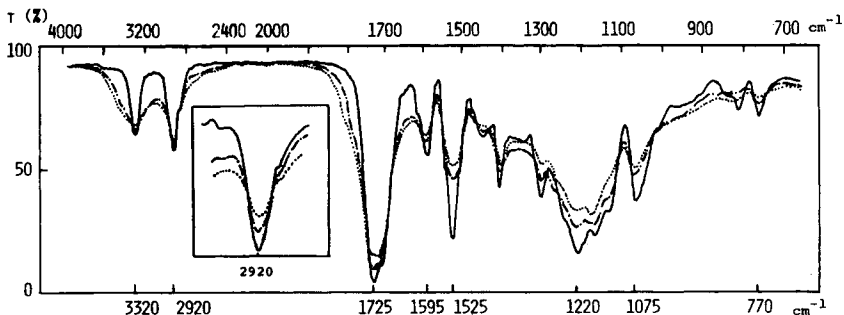

Fig. 6. Changes in the infrared absorption spectra of polyurethane (irradiated without a glass filter, circa 0.04-mm thickness). ——— = original spectrum of polyurethane; - - - - - = spectrum of 30-hr photo-irradiated polyurethane; . . . . . = spectrum of 30-hr photo-irradiated polyurethane containing Sn acetylacetonate (0.5 wt.-%).
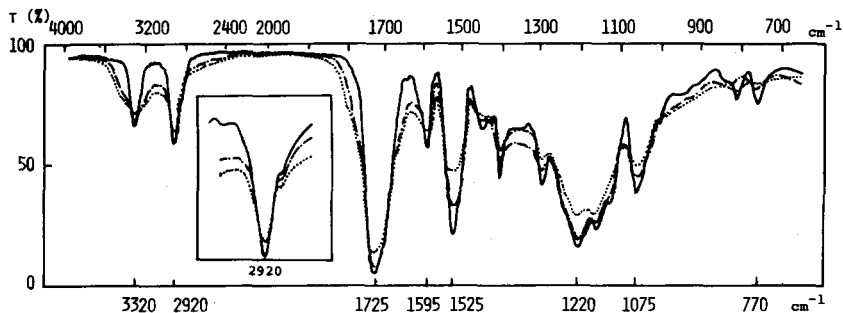
Fig. 7. Changes in the infrared absorption spectra of polyurethane (irradiated with a glass filter; wavelength >3000 Å, circa 0.04-mm thickness): —— = original spectrum of polyurethane; ‐ ‐ ‐ ‐ ‐ = spectrum of 40-hr photo-irradiated polyurethane; . . . . . = spectrum of 40-hr photo-irradiated polyurethane containing Sn acetylacetonate (0.5 wt.-%).

glass filter (wavelength is longer than 3000 Å), the changes in infrared absorption spectra at 2920 cm^{-1} caused by C—H stretching of the methylene group is less compared with that which takes place without a glass filter.

To clarify the changes in polyurethane structure during the photo-irradiation, the relative intensities of absorption peaks at 1075, 2920, 3400, and 1780 cm^{-1} of the representative polymer were plotted against irradiation times and are shown in Figures 8, 9, 10, and 11, respectively.

Figure 8 shows the changes in infrared absorption peak at 1075 cm^{-1} caused by urethane C–O stretching contiguous to the tetramethylene group. The decay of the absorption peak at 1075 cm^{-1} is enhanced in the presence of Sn acetylacetonate and is scarcely affected by Ni acetylacetonate. The other metal acetylacetonates, such as Co(III), Co(II), Cu, and Ti, which enhanced decrease of mechanical properties also accelerated the decay of the peak. In addition, for all samples the decay of the peak when irradiating without a glass filter was faster than when samples were irradiating through a glass fil-
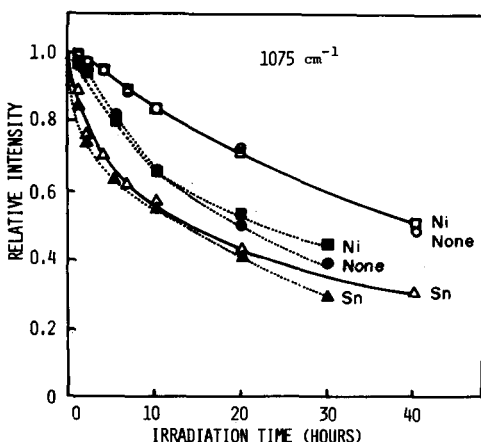

Fig. 8. Changes in the infrared absorption of polyurethane at 1075 cm^{-1} caused by urethane C—O stretching contiguous to tetramethylene group: —— = irradiated without a glass filter; . . . . . = irradiated with a glass filter (wavelength > 3000 Å. O ● = None; △ ▲ = Sn; □ ■ = Ni. Metal acetylacetonates added (0.5 wt.-%).
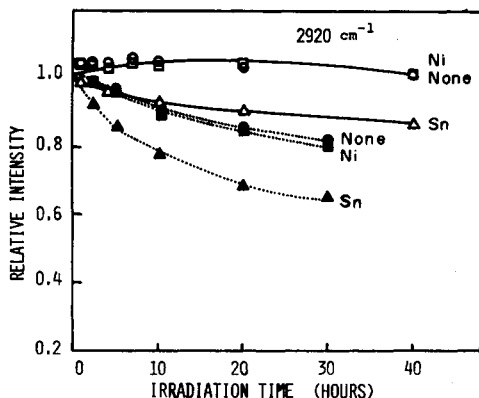
Fig. 9. Changes in infrared absorption of polyurethane at 2920 cm^{-1} caused by C—H stretching of methylene group: ——— = irradiated without a glass filter; ..... = irradiated with a glass filter (wavelength >3000 Å). ○ ● = None; △ ▲ = Sn; □ ■ = Ni. Metal acetylacetonates added (0.5 wt.-%).

ter (wavelength is longer than 3000 Å). Similar phenomena were observed in the decay of 1525 cm^{-1} resulting from N—H deformation (amide II).

Figure 9 shows the changes in infrared absorption peak at 2920 cm^{-1}, caused by C—H stretching of methylene groups. As shown in the figure, in the case of irradiation without a glass filter, the relative intensity of the peak decreases with irradiation times, especially in the presence of Sn acetylacetonate. However, in the case of irradiation through a glass filter, the changes in the relative intensity are very little, especially in polyurethane alone or in polyurethane in the presence of Ni acetylacetonate. The other metal acetylacetonates, such as Co(III), Co(II), Cu, and Ti, which accelerated the photodegradation of the polyurethane, behaved similarly to Sn acetylacetonate. The results apparently imply that methylene groups in the polymer are more stable than urethane groups in the polymer to the photo-irradiation through
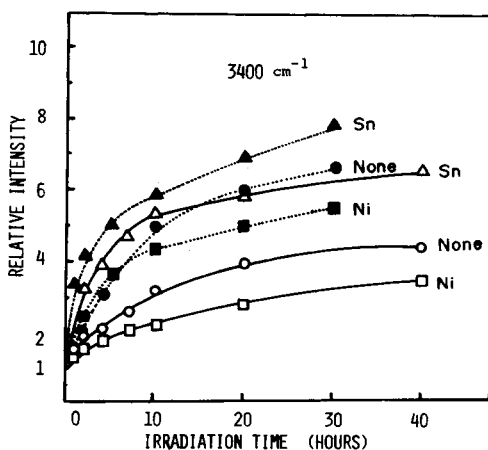

Fig. 10. Changes in the infrared absorption of polyurethane at 3400 cm^{-1} caused by nonbonded NH group: ——— = irradiated without a glass filter; ..... = irradiated with a glass filter (wavelength >3000 Å). ○ ● = None; △ ▲ = Sn; □ ■ = Ni. Metal acetylacetonates added (0.5 wt.-%).
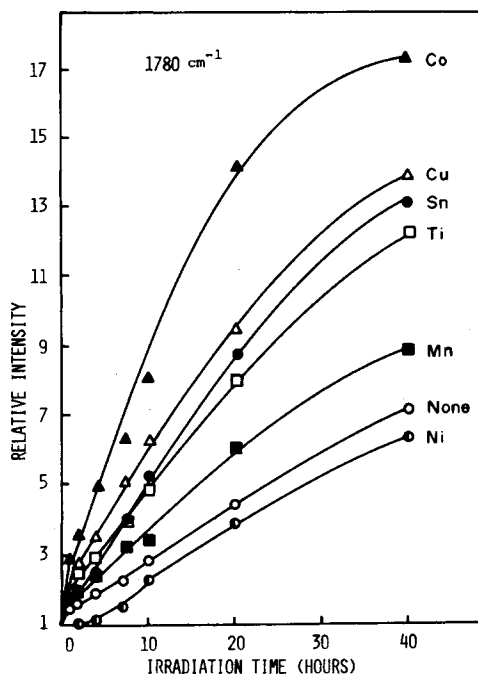
Fig. 11. Changes in the infrared absorption of polyurethane at 1780 cm^{-1} caused by increasing of carbonyl group. Irradiated with a glass filter (wavelength >3000 Å); metal acetylacetonates added (0.5 wt.-%).

a glass filter (wavelength is longer than 3000 Å). It would be reasonable, since the photo-oxidation of polyethylene irradiated through a glass filter was substantially slower than that without a glass filter.[38]

It is generally said that the elastic properties of linear urethane block polymer arise from a hard segment (urethane-based) and a soft segment (ester- or ether-based) and also that the secondary bonding is important in determining the domain structure.[39–40] The typical polyurethane is extensively hydrogen bonded,[41–47] the donor being the NH group of the urethane linkage; and the hydrogen-bond acceptor may be in either the hard urethane segments (the carbonyl of the urethane) or in the soft segments (the ester carbonyl or ether oxygen).

Cooper et al.[48] studied infrared absorption spectral changes of NH vibration in thermal treatment and pointed out that virtually all the NH groups are hydrogen bonded, giving a single peak at 3320 cm^{-1}, and that as the temperature is raised, a high-frequency shoulder develops. This is known as nonbonded NH group and can be used to monitor hydrogen-bond disruption. During the photo-irradiation of polyurethane, similar changes in NH vibration region were observed; namely, the peak at 3320 cm^{-1} decreased, and the region near 3400 cm^{-1} increased with irradiation times. The relative changes of the representative samples at 3400 cm^{-1} were determined and are shown in Figure 10. As shown in Figure 10, Sn acetylacetonate enhances the formation of a free nonbonded NH group. The other metal acetylacetonates, such as Co(III), Co(II), Cu, and Ti, which accelerated the degradation of polyurethane also enhanced the formation of a free NH group. The results may

suggest that the free NH group plays an important role in the mechanical properties of the polymer. Although Cooper et al.[48] explained that the behavior of hydrogen bonding has much less effect on the mechanical properties of polyurethanes, the other reports[42,44,49] claimed the importance of hydrogen bonding for the mechanical properties.

Schollenberger and Stewart[2] reported that the concurrent broadening of the 1700-cm^{-1} band is more pronounced than its decline and suggested the generation of new carbonyl species. As a measure of the extent of the degradation of the polymer, changes in absorption peak at 1780 cm^{-1} were plotted against irradiation times and are shown in Figure 11. As shown in Figure 11, the relative increase in absorption at 1780 cm^{-1} is apparently dependent on the kind of metal acetylacetonates used. Namely, the presence of Co(III), Co(II), Cu, Ti, and Sn acetylacetonates extremely enhances the relative intensity at 1780 cm^{-1}. The tendency fairly correlates with the changes in the physical properties of the polymer.

Ultraviolet and Visible Absorption Spectrum

Changes in the ultraviolet absorption spectra of representative samples in the absence and presence of Sn acetylacetonate are shown in Figures 12 and
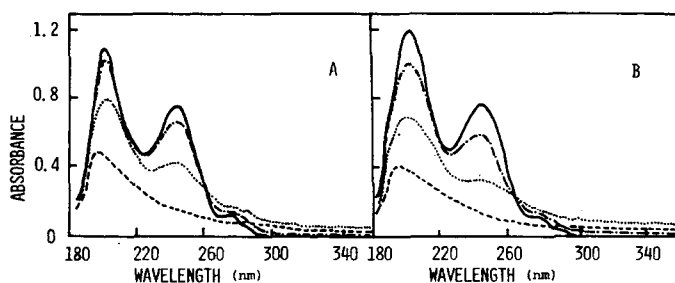

Fig. 12. Changes in the ultraviolet absorption spectra of polyurethane films (2–3 μ): (A) = polyurethane alone; (B) = polyurethane containing acetylacetonate (3 wt.-%). Irradiated time (min): ——— = 0; - · - · - = 20; . . . . . = 90; - - - - = 240.
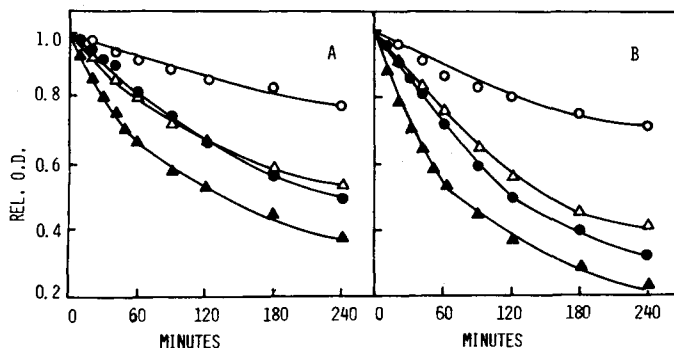

Fig. 13. Changes in the ultraviolet absorption of polyurethane films (2–3 μ). (A) at 202 nm and (B) at 245 nm. Irradiated without a glass filter: –●– = polyurethane alone; –▲– = polyurethane Sn acetylacetonate 3 wt.-% added. Irradiated with a glass filter (wavelength >3000 Å); –○– = polyurethane alone; –△– = polyurethane Sn acetylacetonate 3 wt.-% added.
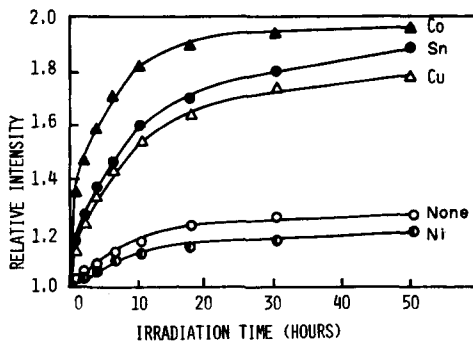
Fig. 14. Changes in the ultraviolet-visible absorption of polyurethane films at 500 nm (0.1 + 0.01 mm) irradiated with a glass filter (wavelength >3000 Å); metal acetylacetonates added (0.5 wt.-%).

13. As shown in Figures 12 and 13, the decay of absorption peaks at 202 and 245 nm, of urethane groups in the polymer is enhanced by the presence of Sn acetylacetonate. The plot of these absorption intensities on incremental photo-exposure obviously shows the acceleration effect of Sn acetylacetonate. Furthermore, the rate of the decay is retarded by photo-irradiation through a glass filter. The changes in the absorption peaks were also largely dependent on the metal acetylacetonates used; and Co(III), Co(II), Cu, and Ti acetylacetonates accelerated the decay.

A deepening color of the photo-irradiated polyurethane sample which changed from colorless to yellow to amber was also observed. It is reported[2,3,23] that the development of quinoneimide structure that develops in auto-oxidized urethane chain is also chromophore responsible for the yellowing of the polymer. The deepening color of the exposed polymer sample can be easily followed by the measurement of visible spectrum of the polymer. Figure 14 shows the relative increase in the optical density at 500 nm
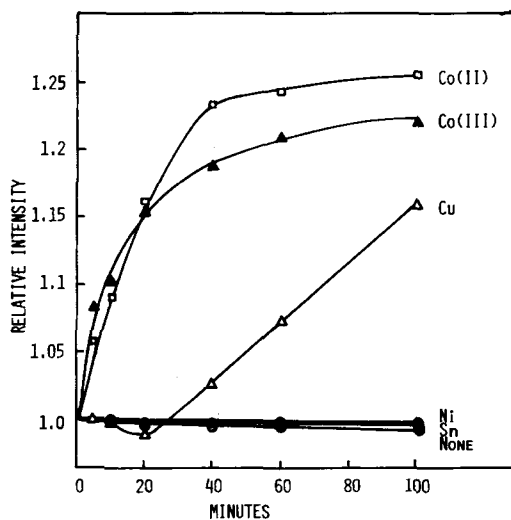

Fig. 15. Changes in the visible asorption of polyurethane films at 500 nm (0.1 ± 0.01 mm). Heat treatment at 120 ± 0.5°C in atmospheric oven.

during the photo-irradiation of the polyurethane in the absence, and presence, of metal acetylacetonates. Figure 14 supplements the information of the results mentioned above: Namely, the acceleration effect of Co(III), Cu, and Sn acetylacetonates and the independent or retardation effect of Ni acetylacetonate are clearly demonstrated.

Effect of Heat Treatment

As mentioned above, the mechanical properties of unirradiated polyurethane films containing Co(III), Co(II), and Cu acetylacetonates were extremely inferior to that of pure polymer. Thermal effect during the curing process seems to be one of the most probable reasons for the degradation of the polymer. In order to elucidate the assumption, heat treatment of uncured polymer film was carried out at 120°C and the changes in visible spectra were measured. Figure 15 shows the relative increase in the optical density at 500 nm during the thermal treatment at 120°C in an atmospheric oven. By the thermal treatment the relative increase in the optical density at 500 nm is enhanced by the presence of Co(III), Co(II), and Cu acetylacetonates. However, the presence of Ni and Sn acetylacetonates is independent at all in the thermal treatment, and no increase in optical density at 500 nm is observed so well as pure polymer within 100 min.

Study of the detailed mechanism of the photodegradation of polyurethanes catalyzed by metal acetylacetonates is going on at present, and the results will be published in the future.

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