

Photoacoustic Study of UV, UV-Thermal, and Weathering Degradation of Rigid Foam Polyurethane

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Synopsis

Degradation of polyurethane samples by UV, combination of UV-thermal, and natural weathering were studied by photoacoustic spectroscopy. This study reveals that degradation of polyurethane could be initiated at a relatively low temperature of 40°C and low UV dosage. It was also found that the effect of heat is more pronounced than the effect of UV. The reaction mechanism of polyurethane degradation is fully in agreement with photoacoustic absorption spectra.

INTRODUCTION

Polyurethanes are widely used by industry due to their toughness, resistance, and other properties. Study of these properties, however, revealed that polyurethanes can be easily affected by UV and heat energies. For example, Lappin¹ and Fox² reported that polyurethane is highly affected by the UV radiation especially with the two lines 254 and 310 nm. They indicated that the main damage occurs through the scission of C—H, C—C, C—O, and C—N in the urethane groups. Fox² proposed a model for degradation by which free radicals migrate from the surface to the bulk through carbon chain. Allen and McKell³ and Ranby and Rabek⁴ reported the formation of conjugated structure and the formation of both monoquinone and diquinone imide as a result of oxidation.

The same effect has been also reported by Schollenberger and Stewart.⁵ They gave evidence that the polyurethane photosensitivity is due to an aromatic diurethane bridge structure which autooxidizes to quinone linkage during photodegradation resulting in discoloration and mechanical changes. Osawa et al.^{6,7} reported degradation associated with cross-linking as a result of UV irradiation.

Grassie et al.⁸⁻¹⁰ and other authors^{11,12} studied thermal degradation at relatively high temperature (>200°C). They reported degradation in the main polyurethane chain. Recently, Abu-Zeid et al.¹³ reported polyurethane degradation at 60°C. This finding is rather interesting since polyurethane is widely used as thermal insulation materials and in a hot climate such

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as that of Kuwait temperature during summer can easily reach 55°C. Abu-Zeid et al.¹⁴ also reported degradation of processed polyurethane exposed to natural weathering. In their work they investigated a polyurethane sample which had been used as thermal insulation material for roof insulation. The sample was weathered for almost 1 year. They showed that the diurethane bridge is autooxidized first to mono-quinone-imide structure and then to a diquinone-imide structure under the effect of UV or heat radiation. In their work Abu-Zeid et al.^{13,14} used photoacoustic spectroscopy technique. This technique has been proved to be most suitable for such studies. Although conventional spectroscopic techniques such as IR and UV-visible spectroscopies reveal very useful informations on photo- and thermal degradation of polyurethane,⁵ photoacoustic technique provides several distinct advantages specially in the study of solid samples such as polyurethane. The spectrum of a solid sample can be obtained without changing its form to a thin film, pellet, or solution as required by other spectroscopic techniques. Even completely opaque or transparent sample can be studied non-destructively. Photoacoustic spectroscopy is also immune to light scattering or reflection from sample surfaces.

In this article we used photoacoustic spectroscopy for further studies of polyurethane photodegradation and the combination of photo- and thermal degradation. We also studied a controlled weathering degradation of polyurethane samples.

EXPERIMENTAL

Samples and Samples Preparation. Polyurethane rigid foam formed by the reaction of 1,4-butane diol and methyl-bis-(4-phenyl-diisocyanate) was used in this experiment. Identical samples $2 \times 5 \times 3$ mm were prepared and kept in light tight box. The dimensions of these samples are identical with the dimension of the photoacoustic sample holder.

UV Irradiation. Spectra Physics CW Ar Ion Laser Model 171A was used for UV irradiation at 335 nm wavelength and 0.5 W power. The samples were irradiated for 1, 2, 3, 4, and 5 min. No discoloration appears for irradiation time less than 3 min. Discoloration, starts to appear at 4 min of exposure. For each of the above exposure times, three identical samples were prepared and kept in a light tight container for analysis.

Combination of UV and Thermal Irradiation. Polyurethane samples were heated at different temperatures (30–80°C) in a controlled oven and at the same time exposed to UV irradiation from Ar Ion laser (335 nm, 0.5 W) for 15 min. For each temperature (30°C, 40°C, 50°C, 60°C, 70°C, and 80°C) three identical samples were also prepared and stored in a light tight container.

Samples Weathering. Polyurethane samples were naturally weathered during summer for periods of 30, 59, and 99 days. All samples were strongly discolored.

Photoacoustic Spectrometer. The detailed description of the photoacoustic set up is published elsewhere,¹³⁻¹⁶ and the reader may refer to it. The source of excitation used in this experiment was a 1000 W xenon lamp. Any variation in the lamp intensity is automatically compensated by the

pyroelectric detector. The spectral range of this equipment is from 200 to 2620 nm at any modulated frequency between 10 Hz to 2 kHz and at any scanning rate from 1 to 200 nm/min. The modulation frequency used in our experiment is 40 Hz which was found to be the optimum frequency for the photoacoustic spectrometer. The sample cell is made of stainless steel and accepts $2 \times 8 \times 2$ mm samples. The exit slit of the light scanning monochromator was 2 mm which results in an 8-nm resolution. Carbon black was used as a reference against which all the spectra were normalized. Air was used as the coupling medium between the sample and the microphone. The equipment is completely controlled and operated by a microprocessor.

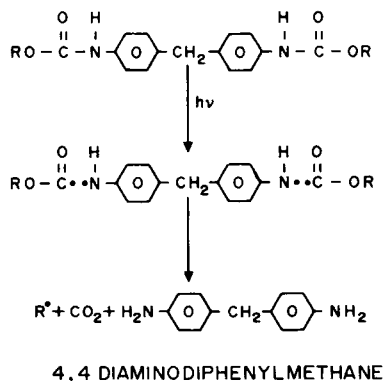
In all figures $(S-B)/R$ was plotted vs. the wavelength, where S is the PAS of the treated sample, B is the PAS of identical but nontreated sample, and R is the PAS of the reference sample (carbon black). $(S-B)/R$ gives the net changes that might take place during samples degradation. We have to mention here also that each recorded spectrum is in fact the average of three samples prepared in the same way and subjected to the same conditions to insure a good representativity of data.

RESULTS AND DISCUSSION

The PAS of UV irradiated samples in solid phase exposed for 2, 3, 4, and 5 min were measured. Since the measurements are for solid polyurethane samples, one might expect a shift in PAS signal to longer wavelength part of the spectrum and the nonexistence of a solvent effect.

Figure 1 shows the PAS of a polyurethane sample exposed for 4 min to UV radiation where discoloration was observed. The recorded PAS in the short wavelength at the UV range 190–200 nm is assigned to the $\pi-\pi^*$ transition, which indicates the formation of conjugated carbonyls, aldehydes, or double bond systems such as butadiene.¹³ Irradiation of polyurethane in air gives rise to the formation of diamine and evolution of carbon dioxide¹⁷: The PAS of the diamine was found to exhibit two maxima¹⁸

SCHEME - I



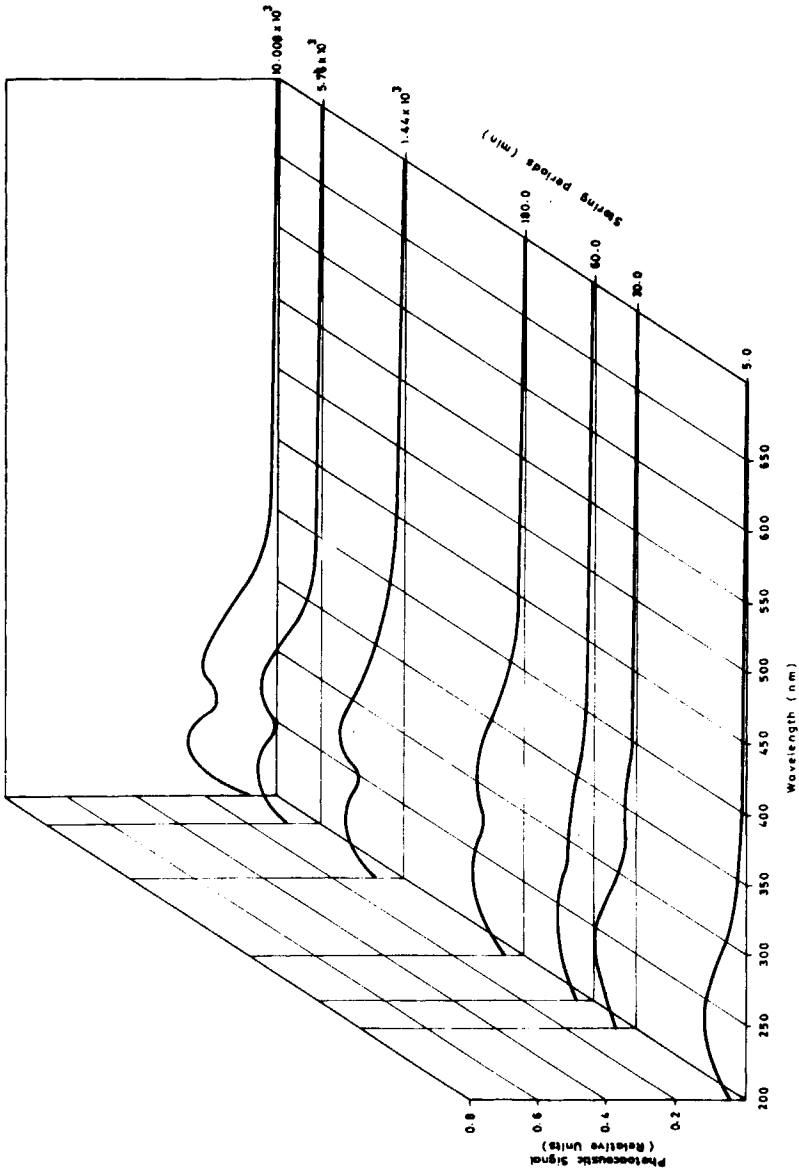
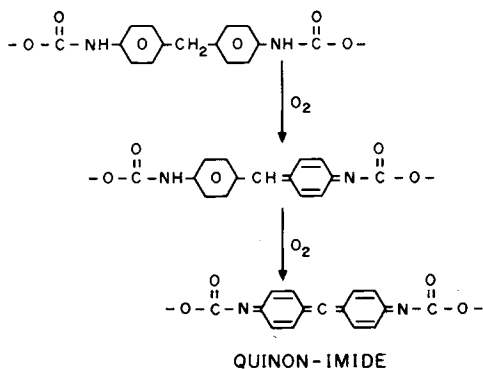


Fig. 1. Photoacoustic spectra of a rigid foam polyurethane sample exposed to UV irradiation for 4 min as a function of the storing time.

at 245 and 290 nm with a shoulder extending to around 325 nm. Simultaneously irradiating polyurethane in air leads to photooxidation and results in formation of a light brown products. This product is noted as quinone-imide¹⁴:

The formation of quinone-imide gave rise to PAS absorption at 400–500 nm and increased with both increasing irradiation and increasing storing

SCHEME - II



time. The formation quinone-imide and diamine is not restricted to long UV exposure times but might appear also at a relatively short irradiation time as evidenced in Figure 2. In this figure the irradiation was 2 min at which no discoloration could be observed visually. It is, however, clear that both quinone-imide and diamine are developed especially at longer storing time.

Furthermore, a combination of UV irradiation and heat will increase the degradation rate of polyurethane since thermal degradation is more effective than the photodegradation as seen in Figure (3). This confirms our previous finding,¹⁴ in which we indicated that UV degradation is restricted to the surface of the sample while thermal degradation penetrated deeper into the sample. Therefore, in the case of the combination effect of UV and heat one would expect that the heat effect on the polyurethane sample is more pronounced and it could overshadow the effect of UV.

The PAS recorded under these conditions suggested the formation of methyl-bis-(4-phenyl diisocyanate) (MBPI) which is the basic compound used in preparation of polyurethane.¹³ MBPI was found to decompose further in the presence of water moisture to form 4,4'-diaminodiphenyl-methane.¹³ The PAS of this compound was found to be peaking with two maxima at 245 and 290 nm, with extended shoulder to around 325 nm. It was noticed that the peaks at 245 and 290 nm increase with storing time and temperature. On the other hand, MBPI might further react with the above diamine to form diphenyl urea¹³ which is peaking at 265 nm with an extended tail¹⁸ to a wavelength of 300 nm. Simultaneously thermal oxidation of polyurethane has occurred and resulted in formation of quinone imide which gives rise to a PAS absorption at 400–500 nm. It is clear from Figure 3 that the

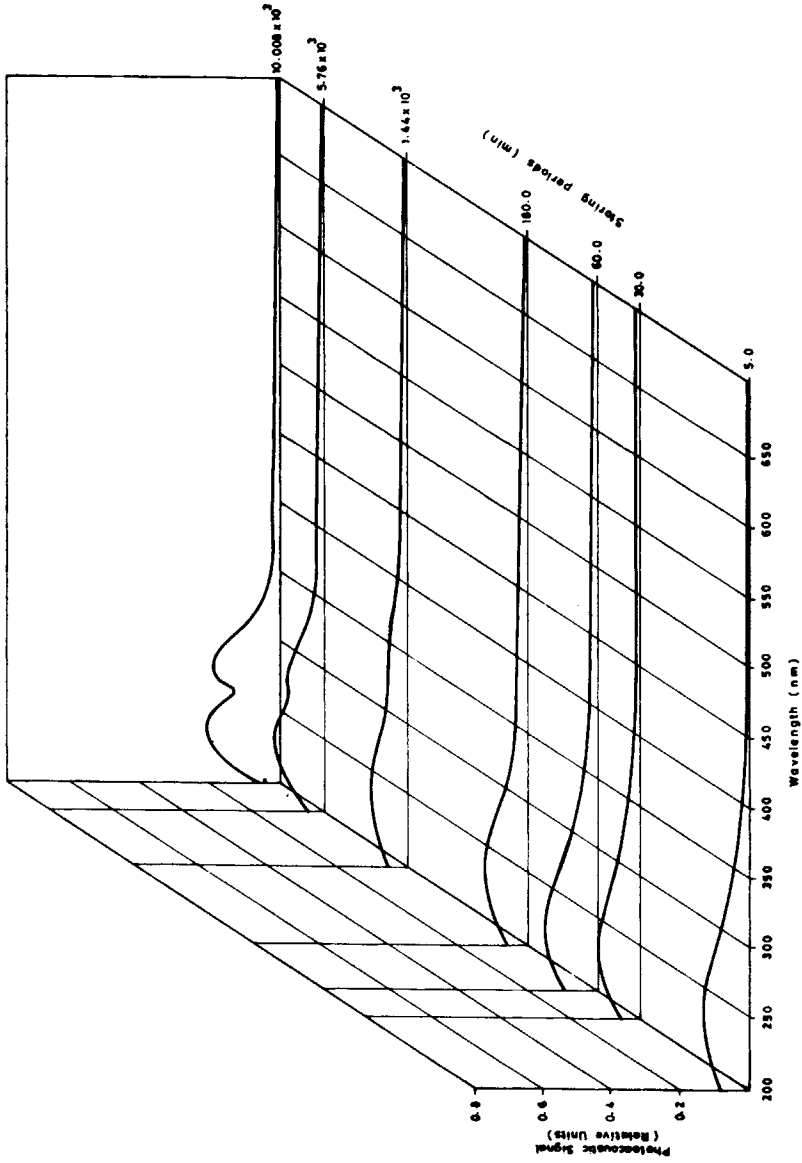


Fig. 2. Photoacoustic spectra of a rigid foam polyurethane sample exposed to UV irradiation for 2 min as a function of the storing time.

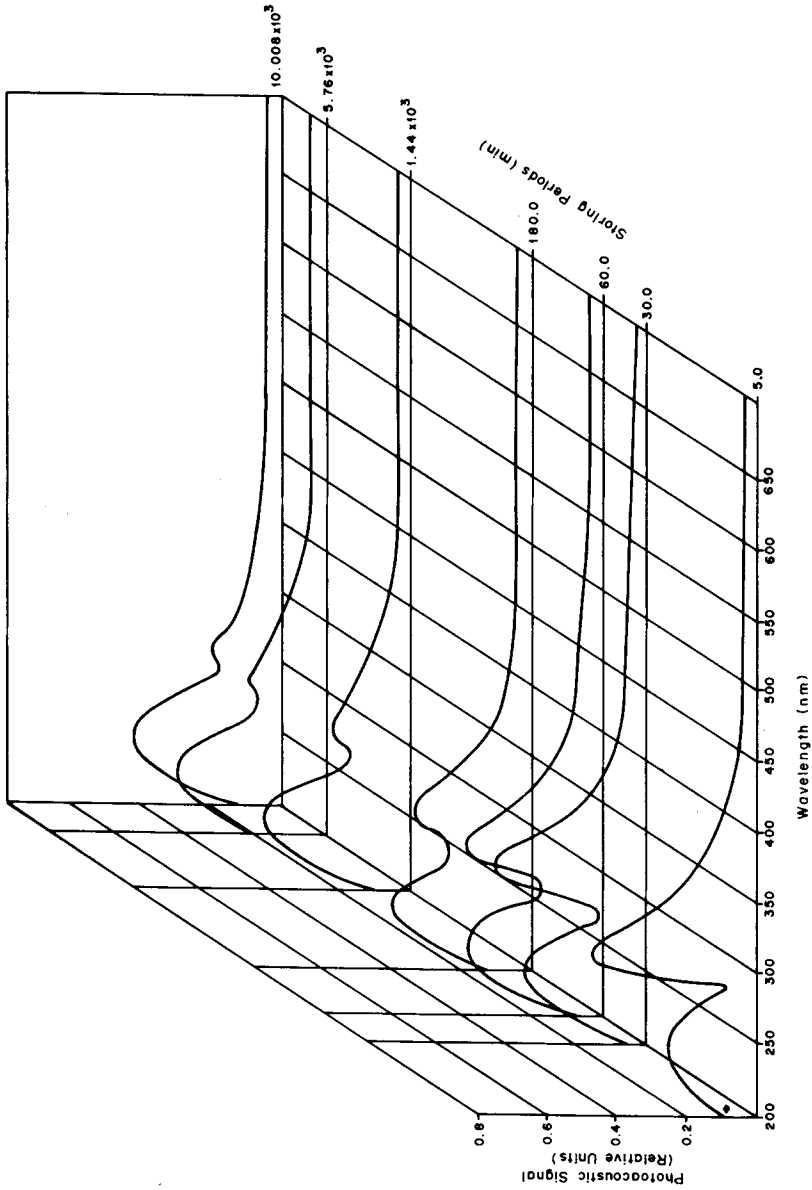


Fig. 3. Photoacoustic spectra of a rigid foam polyurethane sample heated at 70°C for 15 min and at the same time exposed to UV irradiation as a function of the storing time.

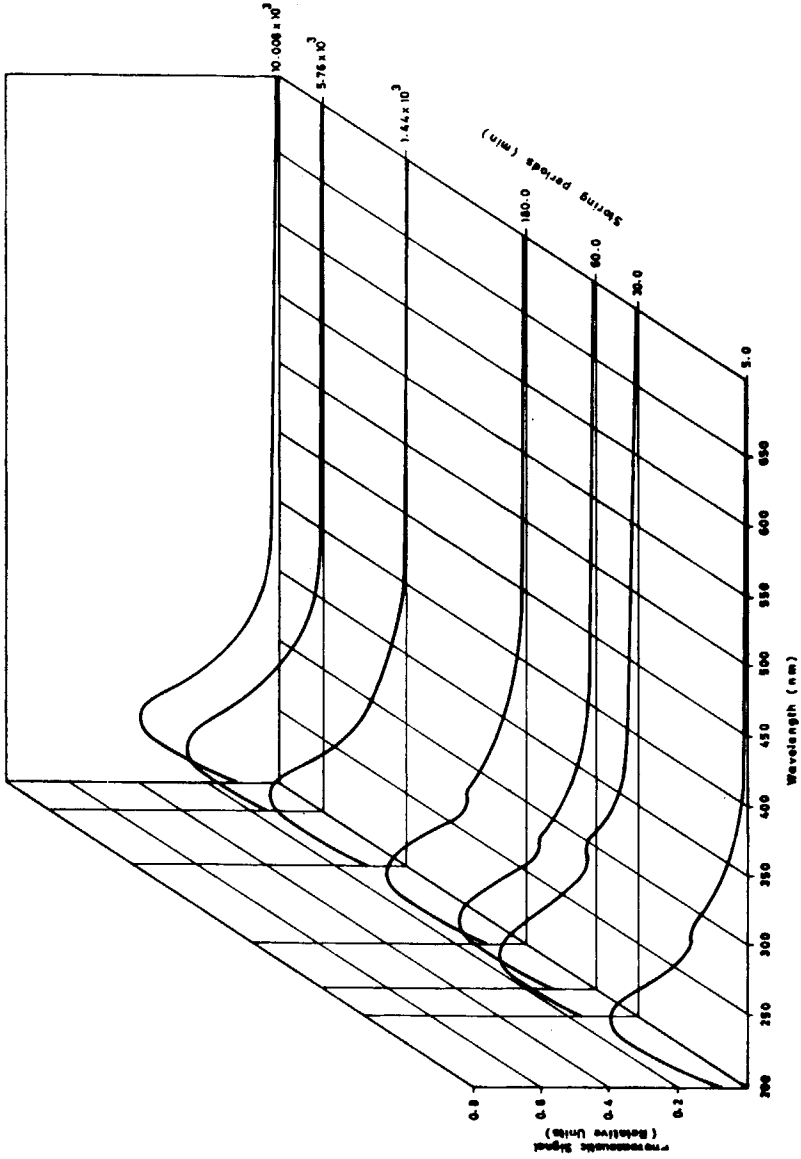


Fig. 4. Photoacoustic spectra of a rigid foam polyurethane sample heated at 40°C for 15 min and at the same time exposed to UV irradiation as a function of the storing time.

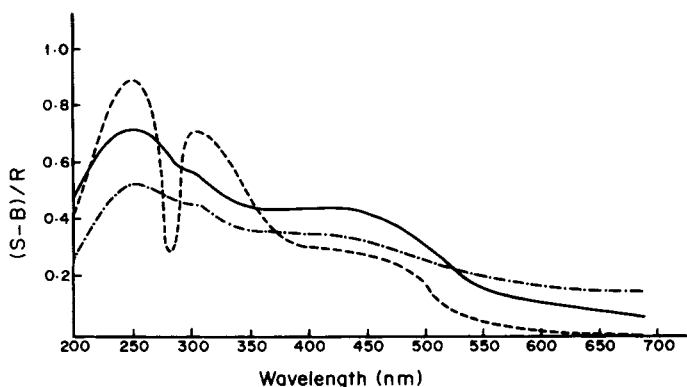


Fig. 5. Photoacoustic spectra of naturally weathered polyurethane sample for: (—) 30 days; (---) 59 days; (- · -) 99 days.

peaks characteristic of the diamine dramatically decrease with storing time and that might be due to the formation of diphenyl urea from the reaction of MBPI with diamine. Very little formation of diamine was observed at relatively low temperature as evidenced in Figure 4. Figure 5 shows the PAS of naturally weathered polyurethane samples exposed for 30, 59, and 99 days during summer. It again displays the same structure previously noticed in the case of combination of UV-thermal degradation, but more discoloration was observed. This was confirmed by a strong PAS absorption at the wavelength of 400–500 nm due to the formation of quinone-imide.¹⁴

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