

STUDY OF NATURAL WEATHERING OF POLYURETHANE RIGID FOAM BY PHOTOACOUSTIC SPECTROSCOPY

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Summary

Photoacoustic spectroscopy was used to obtain the spectra of polyurethane rigid foam samples in powder and solid forms. This technique appears to be extremely efficient for studying optically opaque samples and can offer useful applications in such practical problems as the degradation of naturally weathered polyurethane.

1. Introduction

Although several conventional spectroscopic techniques have revealed useful information on the mechanism of polymer degradation, our recent studies indicate that photoacoustic spectroscopy (PAS) offers distinct advantages. Using PAS, we were able to obtain the spectrum of solid or powder polyurethane samples without changing them to liquids, thin films or pellets as is usually required. It is perhaps the only technique that can provide spectra of such opaque samples. The PAS technique is also very fast and sensitive to sample constituent changes. It is unique in that it provides an optical depth profile, and it is immune to light scattering or light reflection. These and other advantages indicate that PAS is a very promising technique for efficient and cost-effective studies of degradation. The study of the natural weathering of polymers under the severe weather conditions of Kuwait emphasizes important implications for the development of polymer technology, especially with regard to those polymers used in insulating materials.

The theory of photoacoustic studies of solid samples has been worked out in detail by several scientists [1 - 3]. The sample under investigation is irradiated with frequency-modulated monochromatic radiation. Part of this monochromatic radiation is absorbed by the sample and produces a temper-

ature fluctuation in the sample coupling medium at the modulated frequency. As a result, pressure waves are generated in the coupling medium in contact with the sample surface. These pressure waves are then detected by a sensitive microphone to indicate the power absorbed by the sample at the wavelength of the incident radiation.

2. Experimental details

In this study we used two polyurethane rigid foam samples based on methylene di-isocyanate which is extensively used as an insulating material in Kuwait. One sample had been exposed to Kuwait weather for approximately 1 year, and the other was fresh and unexposed. The exposed sample was subjected to natural weathering conditions which include summer temperatures exceeding 150 °F and subfreezing temperatures in the winter. Added to this are extreme sand and dust storms that blow frequently throughout the year, forming a thick layer of suspended particles in the air several kilometres above sea level. Three distinct layers were identified in the exposed sample and were carefully separated. The layers had almost completely different colours, indicating different degrees of degradation. The layers were crushed in liquid nitrogen to particles of approximately the same size which were then dried. This treatment is very important as the photoacoustic signal is dependent on both the size of the particles and the state of the sample. The unexposed sample was prepared in the same way. One additional sample was obtained by cutting a thin layer from the most

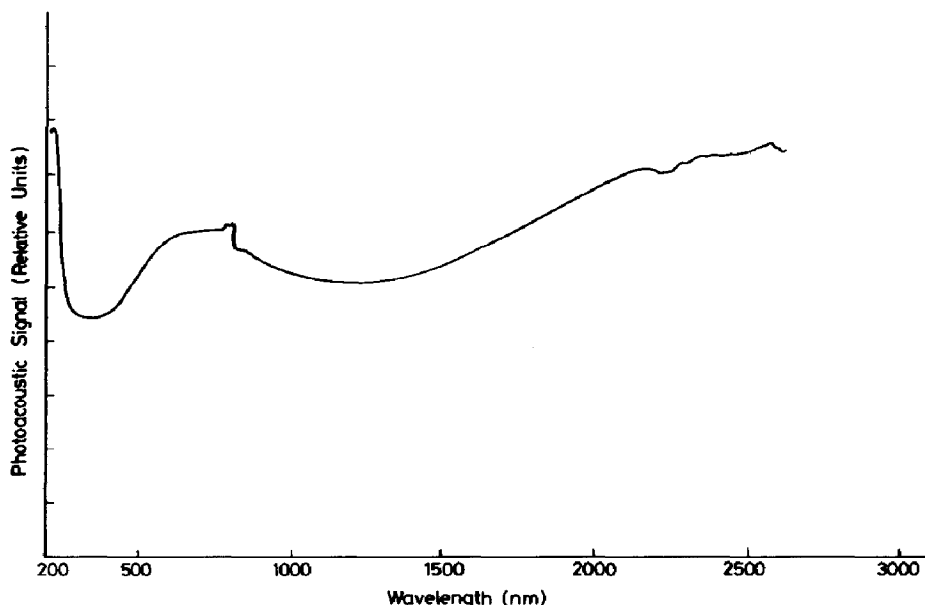


Fig. 1. Photoacoustic spectrum of carbon black.

degraded (*i.e.* the most exposed) part of the exposed sample, and this was used in its solid form.

The photoacoustic spectrometer has been discussed in earlier publications [4, 5]. It utilizes a 1000 W xenon arc lamp as a source of excitation. The sample holder is made of fused silica and can accept samples of dimensions 4 mm × 8 mm × 2 mm in liquid, solid or powder forms. Air was used as the coupling medium rather than helium owing to the strong signal obtained from our samples. Carbon black was used as a reference standard (Fig. 1). The wavelength range of this equipment extends from 200 to 2620 nm utilizing three different gratings that blaze at different parts of the spectrum. The modulation frequency range is between 10 Hz and 2 kHz. The optimum frequency for our equipment was found to be 40 Hz. The equipment is controlled and operated by a microprocessor.

3. Results

The photoacoustic signal of the three layers of the exposed sample (in powder form) together with that of the unexposed sample at a modulation frequency of 40 Hz is shown in Fig. 2. In this figure curve 1 represents the signal from the fresh unexposed sample which was pale yellow in colour.

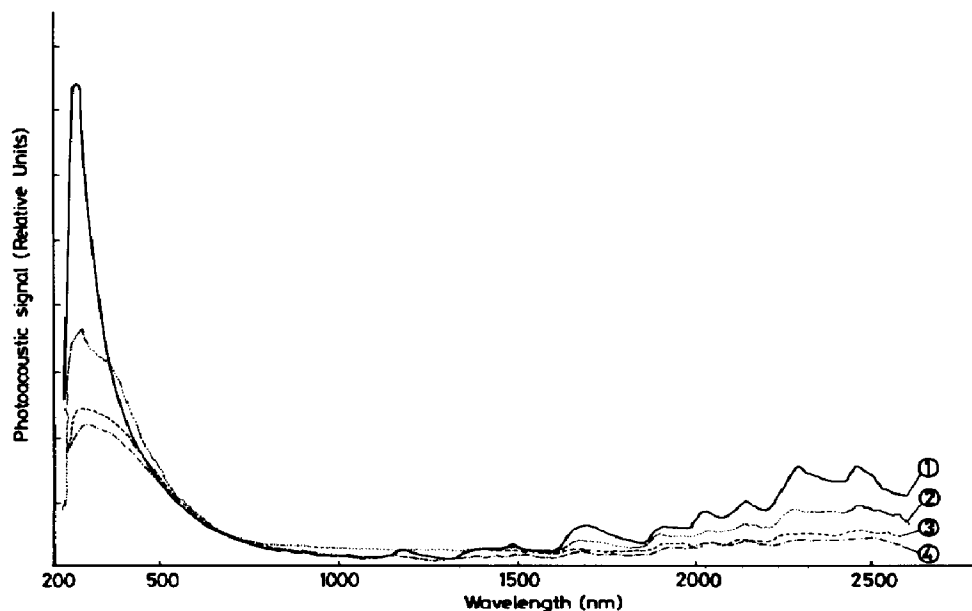


Fig. 2. Photoacoustic spectra of polyurethane: curve 1, the fresh unexposed polyurethane sample; curves 2, 3 and 4, the bottom, middle and top layers respectively of the exposed polyurethane sample.

Curve 2 represents the bottom layer of the exposed sample which was yellowish brown in colour. Curve 3 is due to the signal from the middle layer of the exposed sample which was dark brown in colour. Curve 4 was taken from the top layer of the exposed sample, which was directly in contact with the sunlight and was almost black in colour. Since the photoacoustic signal is related to the optical absorption coefficient of the sample [1], the photoacoustic spectrum is actually the absorption spectrum of our sample relative to that of carbon black.

The photoacoustic spectra shown in Fig. 2 cover three different regions: UV, visible and red-near-IR. The UV part of the photoacoustic spectrum which peaks around 270 nm shows a decline in intensity from curve 1 to curve 4. This is an indication of loss of aromatic urethane structure, *i.e.* the part of the polyurethane that absorbs UV (the chromophore) is broken or degraded and the degree of degradation depends on how close each layer is to the direct sunlight. Similar behaviour has been observed by Schollenberger and Stewart [6] using thin (2 - 3 μm) linear polyurethane films subjected to different sunlight exposure periods that ranged between 0 and 154 h. The UV component in sunlight can penetrate a film 2 - 3 μm thick and can cause homogeneous polyurethane degradation throughout the film (depending on the absorbed UV dose) similar to that observed. However, the situation is completely different in our case. We used a sample several centimetres thick, yet we still observed a similar effect. The UV component of sunlight cannot penetrate such a thick sample. The loss of some of the aromatic polyurethane structure in the middle and bottom layers cannot be attributed to the direct UV component of sunlight in our experiment. It was found to be due to a heat effect [7].

The visible part (400 - 700 nm) of the photoacoustic spectrum is perhaps the most interesting of all. A careful look at Fig. 2 shows that the fresh non-exposed polyurethane sample (curve 1) has a sharp peak at around 270 nm. A shoulder is formed at 380 nm in curve 2 and the subsequent curves. Also, there is an overall broadening of the main peak and the developed shoulder which increases in going from curve 2 to curve 4. This effect is clearly shown in Fig. 3, which was obtained by subtracting curve 1 from the rest of the curves after normalizing all these curves to the peak of curve 1. This new structure becomes more pronounced the closer the layer of the polyurethane sample is to the sunlight and is due to quinoid structure formation. The diurethane bridge is autoxidized first to a monoquinone-imide structure and then to a diquinone-imide structure under the effect of UV or heat radiation [8]. The reaction leading to the formation of quinoid in linear polyurethane after it has been subjected to UV has been reported elsewhere [6]. However, our technique is unique in that it is apparently the only way to reveal this phenomenon in the part of the sample which is black and solid. Other conventional spectrometers will not be able to provide any information for a sample of this nature.

The red-near-IR region (700 - 2620 nm) reveals some spectral structure in the region 1400 - 2620 nm. This structure decreases in intensity in a

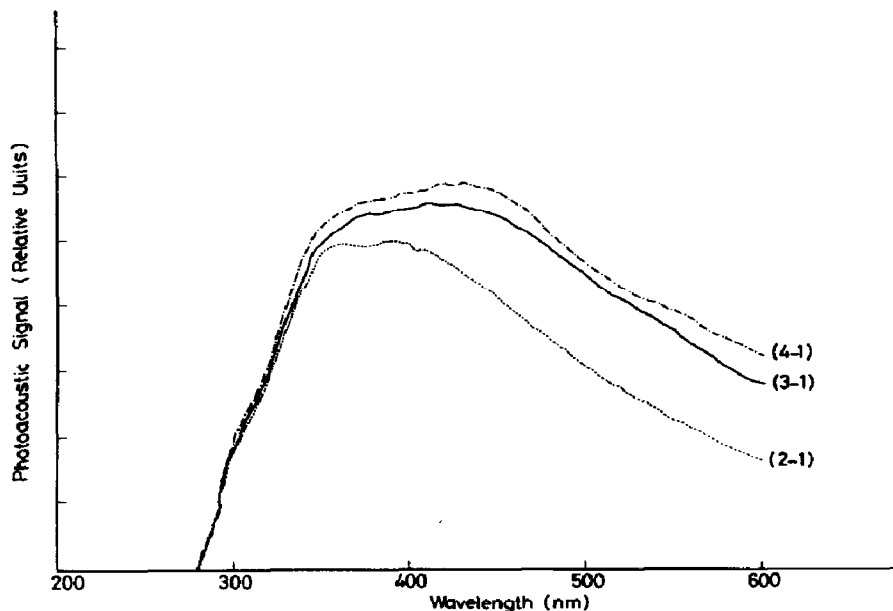


Fig. 3. Photoacoustic spectrum obtained by subtracting curve 1 in Fig. 2 from curves 2, 3 and 4 after normalizing all these curves to the peak of curve 1.

fashion similar to the UV part of the spectrum previously discussed. Again, this could be due to polyurethane degradation. Because of the complexity of the polyurethane molecules and the fact that we do not know what additives and stabilizers were used in the product by the manufacturing company, we were not able to identify the peaks of this part of the spectrum.

The thermal diffusivity [9] for polyurethane at 298.7 K is $3.05 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. At a modulation frequency range between 10 and 200 Hz the corresponding polyurethane thermal diffusion length μ lies between 9.86×10^{-3} and $2.20 \times 10^{-3} \text{ cm}$. This means that μ is very much less than unity. Since our sample is considered to be an optically opaque solid, the optical absorption length μ_B is also very much less than unity. According to the theoretical calculation [1], if μ is less than μ_B the optically opaque sample is also classified as a thermally thick solid. In this case the photoacoustic signal is proportional to $\nu^{-3/2}$ where ν is the modulation frequency in hertz.

Figure 4 shows the photoacoustic spectrum of the solid layer of the exposed polyurethane sample with the most degraded part facing the photoacoustic monochromatic light beam. The modulation frequency was varied between 10 and 200 Hz. The relation between the photoacoustic spectrum and the modulation frequency at the wavelength $\lambda = 290 \text{ nm}$ is shown in Fig. 5. This relation indicates that our sample can be classified as an optically opaque and thermally thick solid.

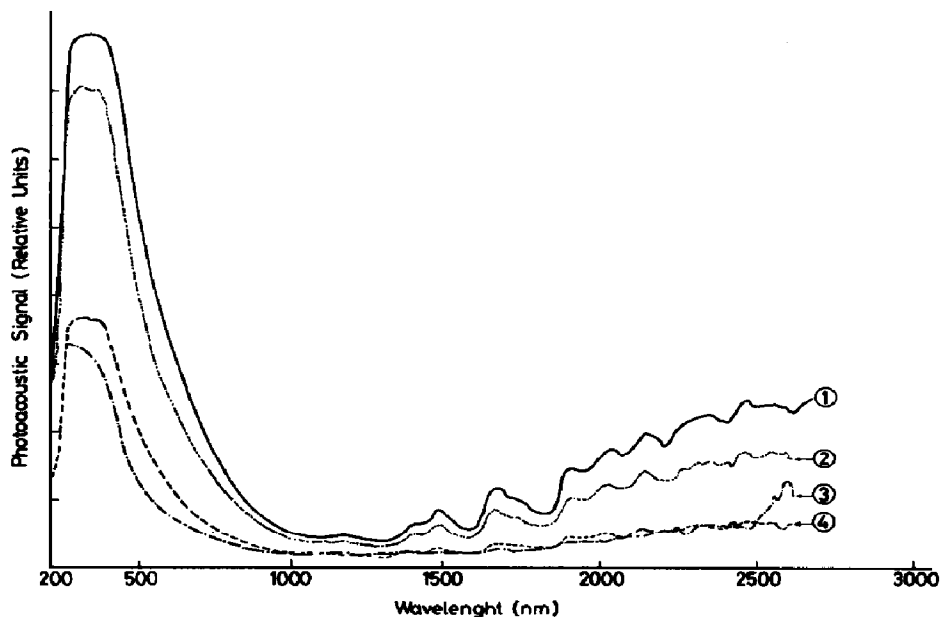


Fig. 4. Photoacoustic spectrum of the exposed polyurethane sample at various frequencies: curve 1, 10 Hz; curve 2, 12 Hz; curve 3, 40 Hz; curve 4, 200 Hz.

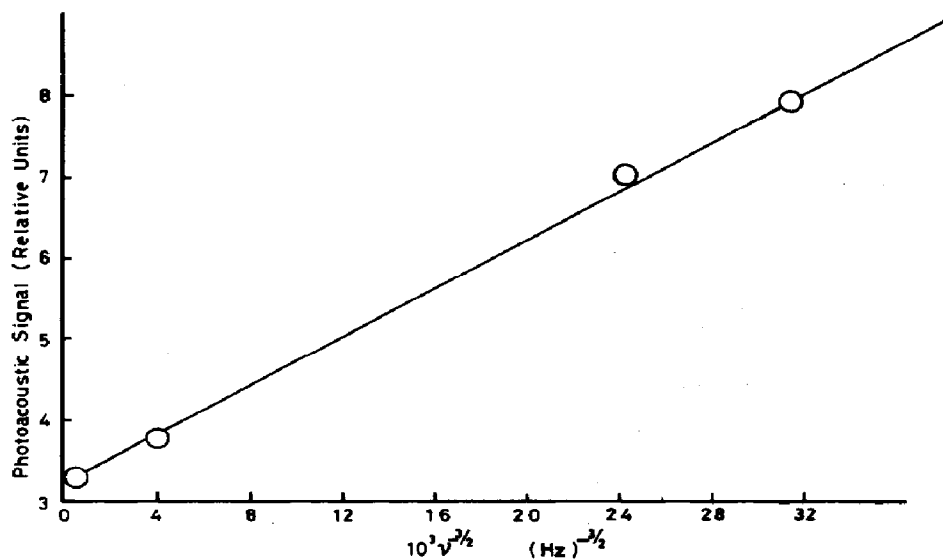


Fig. 5. Dependence of the photoacoustic signal on the modulation frequency at $\lambda = 290 \text{ nm}$.

Acknowledgments

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