Photoacoustic Study of Thermal Degradation of Polyurethane

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Synopsis

Polyurethane rigid foam shows substantial changes in its photoacoustic absorption spectra (PAS) on heating in the presence of air. These spectral changes are due to conjugated structures and quinone–imide formation, formed during degradation. The mechanism of degradation appears to be free radical in nature.

INTRODUCTION

A good deal of information about degradation reactions may be obtained quickly by means of thermal volatilization analysis which has been devised and described by McNeill.[1-3] Furthermore, Grassie and co-workers[4-7] explained in detail the mechanism of polyurethane degradation. Two basic structures were distinguished in commercial polyurethanes, namely, the urethane link itself and a polyether or polyester sequence. The thermal degradation of a series of polymers is described in which increasing amounts of polyester sequences are incorporated into the basic polyurethane structure.[6] In this article the thermal degradation mechanism of polyurethane is followed by photoacoustic spectroscopy.

Although conventional spectroscopic techniques yield very useful information, the photoacoustic technique provides several distinct advantages 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. Completely opaque or transparent samples can be studied nondestructively. Photoacoustic spectroscopy is also immune to light scattering or reflection from the sample.

The photoacoustic phenomenon was first reported by Bell[8] and others[9,10] in 1881. However, the development of this phenomenon for use with solids took place only recently.[11] Since then, considerable theoretical[12] and experimental[13] work has taken place. The basic principle of photoacoustic spectroscopy is that when a modulated monochromatic beam of light falls on the surface of a sample, it excites its molecules. The molecules lose part of their excitation energy in the form of heat through nonradiative processes. This heat causes a modulated pressure wave which propagates in a nonabsorbing coupling medium. The

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pressure wave is then detected by a sensitive microphone to indicate the power absorbed by the sample at the wavelength of the incident radiation.

EXPERIMENTAL

Photoacoustic Spectrometer

The photoacoustic spectrometer used in this work was described in earlier publications.[13–15] A 1000-W Xenon lamp was used as a source of excitation. A pyroelectric detector compensates for any variation in the lamp intensity that might occur during the spectrum gathering. The spectral range of this equipment is from 200 to 2600 nm at any modulated frequency between 10 Hz and 2 KHz and a scanning rate of 200 nm/min. The sample cell is made of high quality quartz and accepts $5 \times 8 \times 2$ mm samples in liquid or solid phases. The exit slit of the light scanning monochromator was 2 mm at which the resolution of the spectrometer is 8 nm. Carbon black was used as a reference against which all the spectra were normalized. Air was used as a coupling medium between the sample and the microphone. The equipment is completely controlled and operated by a microprocessor.

Samples and Sample Preparation

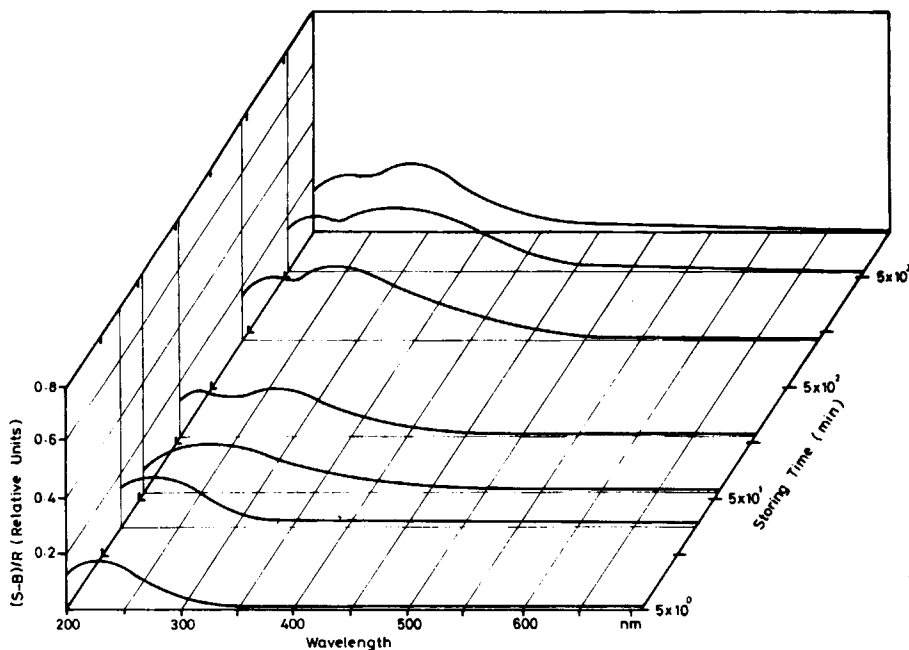Commercial polyurethane rigid foam based on methylbis (4-phenyl diisocy-

Fig. 1. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 60°C as a function of the storing time. The peak between 190 nm and 200 nm is assigned to conjugated carbonyls or aldydes and the peak between 220 nm and 270 nm is assigned to aromatic amines or urea. The shoulder between 270 nm and 320 nm is assigned to aromatic amines or aromatic urea.
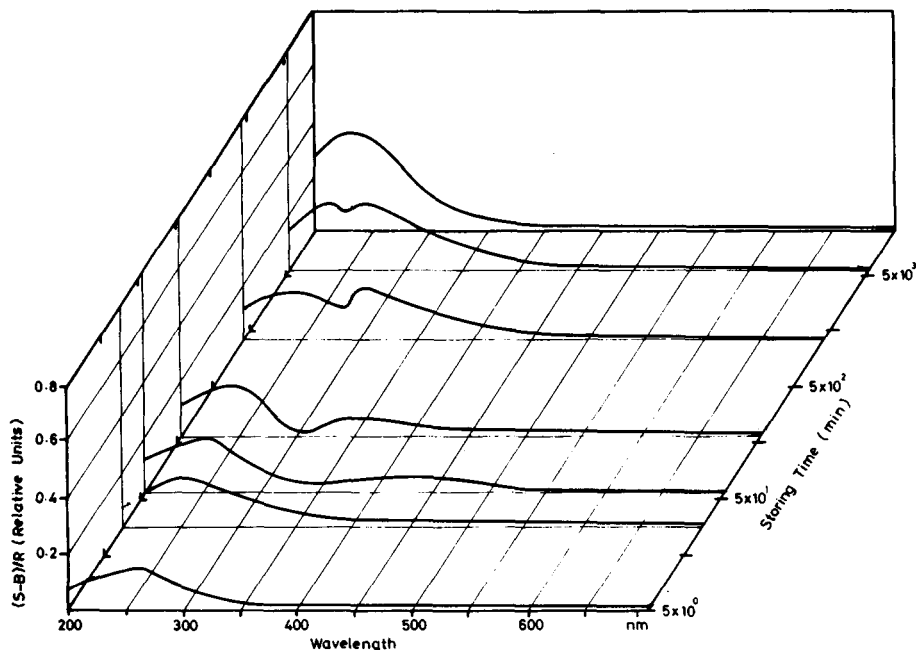
Fig. 2. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 80°C as a function of the storing time. The peaks and their assignments are similar to that in Figure 1 except the peak that is assigned to conjugated carbonyls or aldydes becomes more pronounced.

anate) (MPBI) was used in this experiment as it was delivered by the local industry. Identical samples were then prepared and heated at 60°C, 80°C, 100°C, 150°C, 200°C, and 250°C in air. The spectrum of a fresh (nonheated) polyurethane sample was first recorded and stored as a blank (B) in the memory of the microprocessor. (B) was then subtracted from the spectrum of each heat treated sample (S) to yield the net changes (S-B) in the heat treated sample that might take place as a result of degradation. The microprocessor was then automatically normalized (S-B) against the carbon black reference spectrum (R) to give (S-B)/R signal. The heat-treated samples were used after being stored in air (for different periods of time) at normal pressure and temperature (22°C).

RESULTS

The photoacoustic spectra (PAS) of rigid polyurethane foam heated for 15 min at 60°C, 80°C, 100°C, 150°C, 200°C, and 250°C were all recorded and are shown in Figures 1–6, respectively. The recorded PAS showed a characteristic absorption peak in the UV range at 190–200 nm assigned to the $\pi-\pi^*$ transition indicative of conjugated carbonyls, aldehydes, or double bond systems. The peaks at 220–270 nm are typical aromatic $\pi-\pi^*$ transition of the aromatic chromophores of the amines or the urea which are formed from the decomposition of the polyurethane. The absorption at 270–320 nm is the typical absorption of the $n-\pi^*$ transition of the aromatic amines, aromatic urea, and the base material of polyurethane methylene bis(4-phenyl diisocyanate) (MBPI). It was
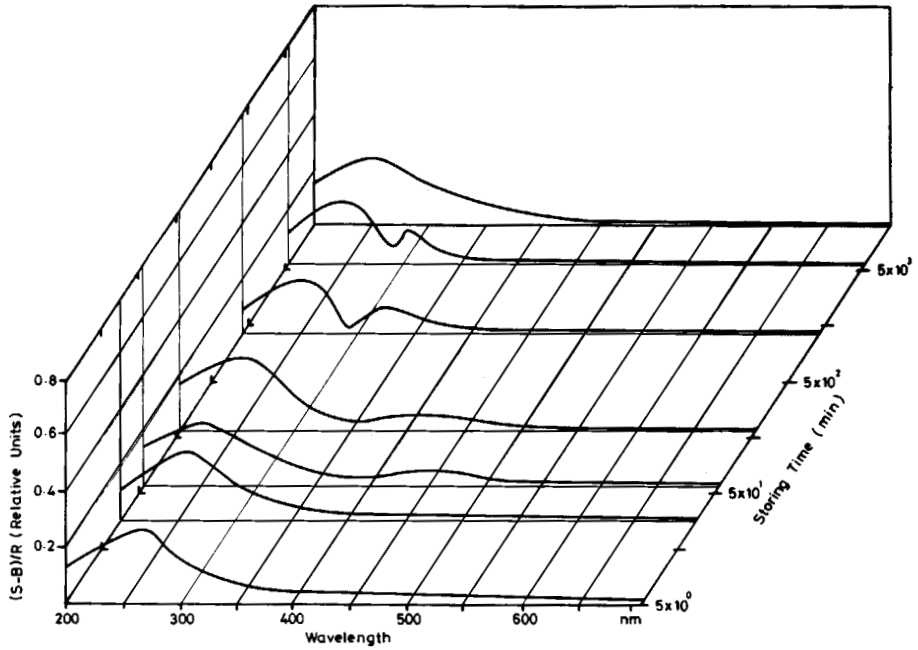
Fig. 3. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 100°C as a function of the storing time. The peaks and their assignments are similar to that in Figure 1, while the conjugated carbonyls peak becomes much more pronounced and overshadows the neighboring peak.
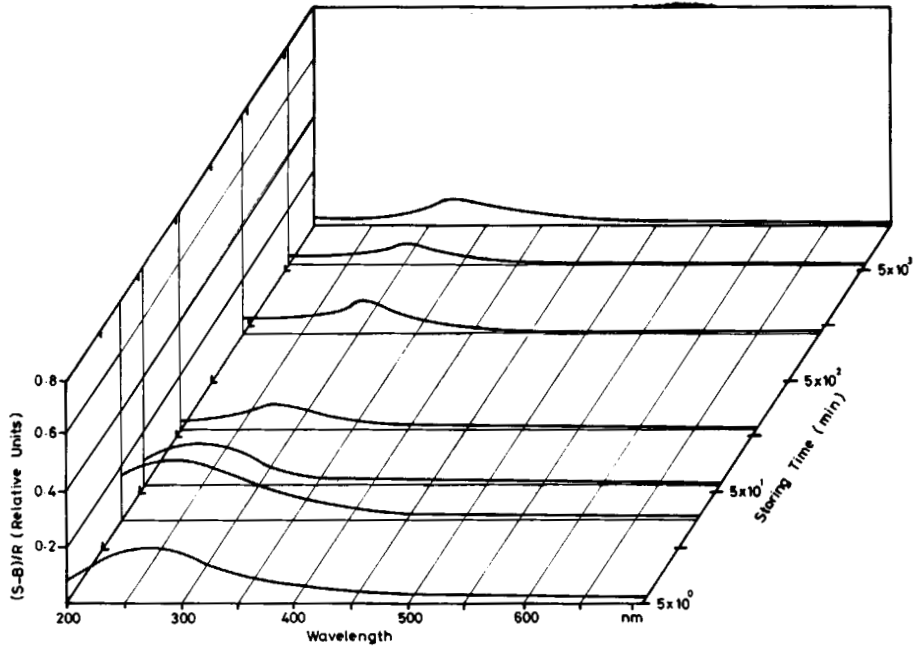

Fig. 4. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 150°C as a function of the storing time. The peak between 190 nm and 200 nm is assigned to conjugated carbonyls or aldydes. This peak disappeared with the storing time while peaks due to the aromatic amines or urea (220–270 nm and 270–320 nm) remain unchanged.
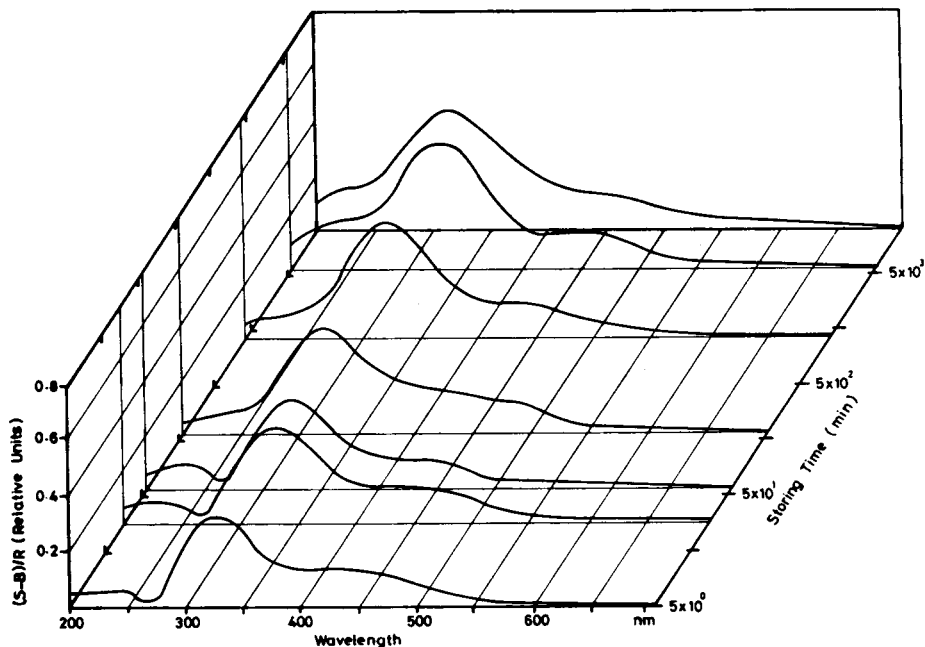
Fig. 5. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 200°C as a function of the storing time. The peaks due to conjugated carbonyls or aldydes (190–200 nm) almost disappear while the peaks due to aromatic amines or urea (220–270 nm and 270–320 nm) become much more pronounced. Another peak at 450 nm with an extended tail to 550 nm appears and is assigned to quinone imide formation.
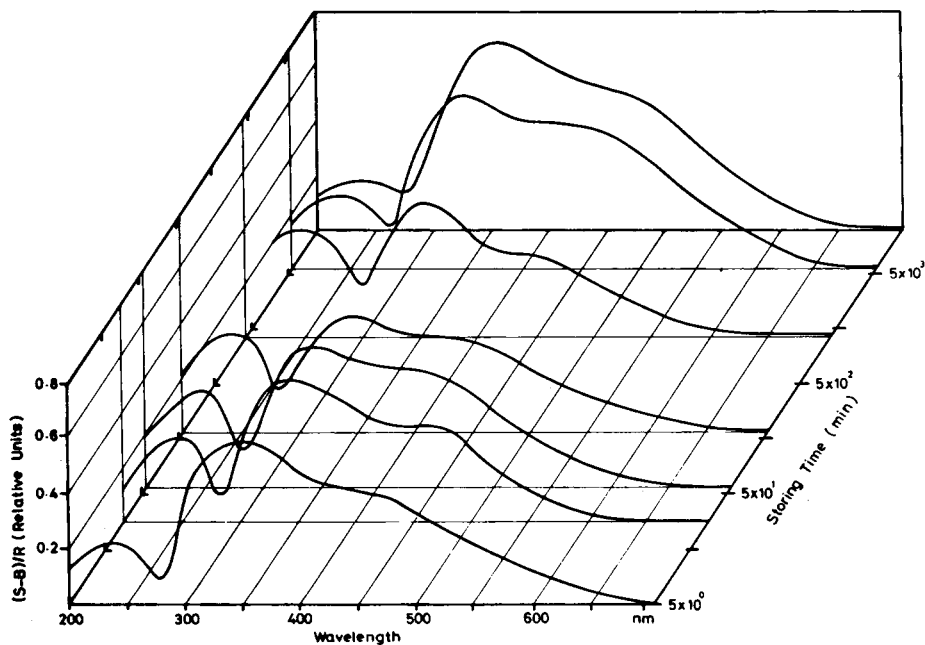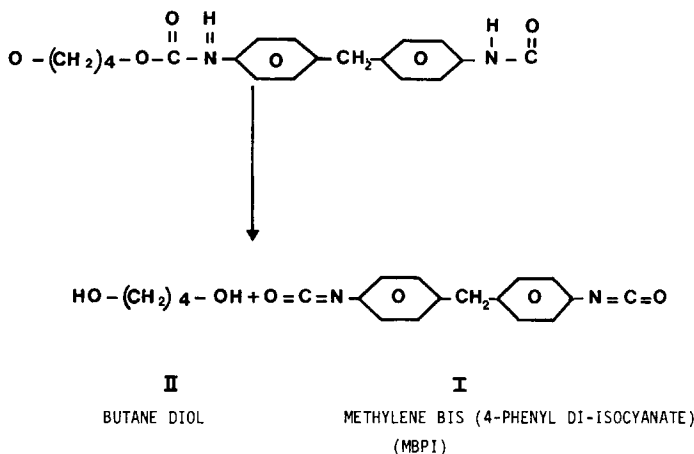

Fig. 6. Photoacoustic spectra of a rigid foam polyurethane sample heated for 15 min at 250°C as a function of the storing time. The peaks and their assignment are similar to that in Figure 5 except all peaks become more pronounced, and the conjugated carbonyl peaks appear again.

noted that this peak becomes the major peak on aging as the aging time and temperature of the polyurethane are increased, as can be seen in Figures 3–6. Simultaneously, several peaks were noted in the visible region at 400–550 nm in the PAS, as the temperature of aging increased as shown in Figures 3, 5, and 6. Those peaks have been assigned to the formation of quinone–imide,[14,16,17] and they are responsible for the highly colored products formed upon the degradation of polyurethane.
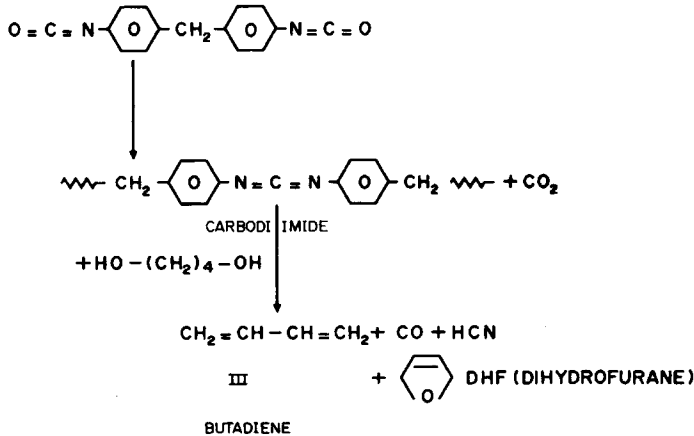
DISCUSSION

The recorded PAS in the shorter wavelengths, in the UV range, suggests the characteristic absorption band of the methyl bis(4-phenyl diisocyanate) (MBPI) which is the basic compound used in preparation of polyurethane. However, peaks at 200–280 nm can be related directly to the formation of the MBPI compound due to the decomposition of polyurethane by heat as shown in the mechanistic Scheme 1.

Scheme 1.

II
BUTANE DIOL

I
METHYLENE BIS (4-PHENYL DI-ISOCYANATE)
(MBPI)

Scheme 2.

CARBODI IMIDE

III BUTADIENE

+ DHF (DIHYDROFURANE)

Scheme 3.

$$O = C = N - \langle O \rangle - CH_2 - \langle O \rangle - N = C = O$$

$$\downarrow H_2O$$

$$HO - \overset{O}{\underset{\parallel}{C}} - \overset{H}{\underset{\mid}{N}} - \langle O \rangle - CH_2 - \langle O \rangle - \overset{H}{\underset{\mid}{N}} - \overset{O}{\underset{\parallel}{C}} - OH$$

$$\downarrow$$

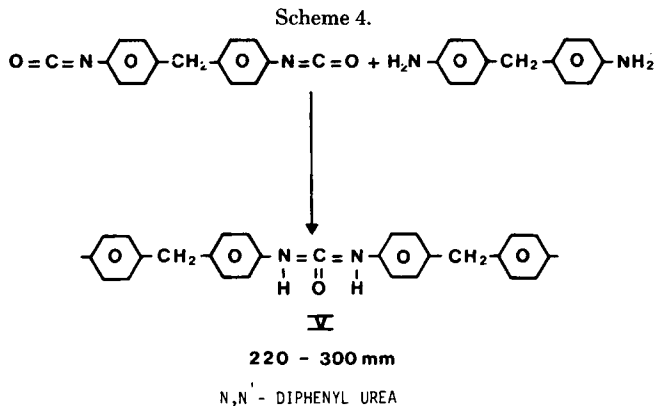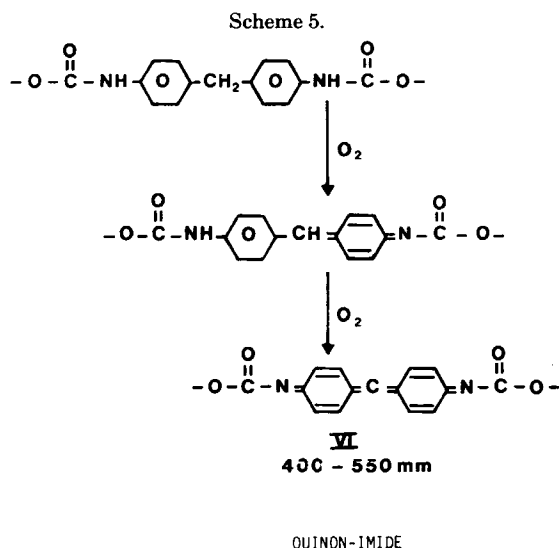$$CO_2 + H_2N - \langle O \rangle - CH_2 - \langle O \rangle - NH_2$$
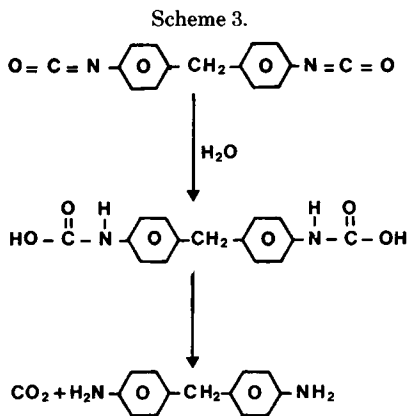
IV

4,4'-DIAMINODIPHENYLMETHANE

It is worth mentioning that the PAS were measured in solid phase which will give rise to a shift in the longer wavelength part of the spectrum and elimination of the solvent effect. On the other hand, the MBPI compound, found to decompose on further heating and in the presence of diols such as (II), will form a range of volatile materials such as CO, HCN and conjugated dienes (III) as in the mechanistic Scheme 2. The PAS of conjugated dienes such as butadiene will lie in the far UV spectra around 190–200 nm, due to the $\pi-\pi^*$ transition. Since we heated the polyurethane in air, any traces of water moisture present will react with (I) to form a diamine and evolution of carbon dioxide[5]—Scheme 3.

The PAS of the diamine (IV) was found to exhibit two maxima[18] at 245 nm and 290 nm with extended shoulder to around 325 nm. However, it was noticed that the peaks at 245 nm and 290 nm rise with aging time and temperature. This can be related to the direct reaction of (MBPI) with water as shown in Scheme 3. On the other hand (MBPI) might react with the diamine formed from the previous step to form diphenyl urea which is peaking at 265 nm with an extended tail to the wavelength of 300 nm as per Scheme 4. Simultaneously, heating of

Scheme 4.

$$O = C = N - \langle O \rangle - CH_2 - \langle O \rangle - N = C = O + H_2N - \langle O \rangle - CH_2 - \langle O \rangle - NH_2$$

$$\downarrow$$

$$\langle O \rangle - CH_2 - \langle O \rangle - \overset{}{\underset{H}{N}} = \overset{}{\underset{O}{C}} = \overset{}{\underset{H}{N}} - \langle O \rangle - CH_2 - \langle O \rangle -$$

V

220 - 300 mm

N,N' - DIPHENYL UREA

Scheme 5.

QUINON-IMIDE

polyurethane in air leads to thermal oxidation of the polyurethane and results in the formation of light brown product. This product is noted as quinone–imide[14] as per Scheme 5. The formation of quinone–imide compound gave rise to a PAS absorption at 400–550 nm.

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