Thermal and Photochemical Stability of an Aromatic Polyurethane

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A polyurethane (PU) based on 4,4'diphenylmethane diisocyanate (MDI), copolyester poly(ethyleneadipate) diol (PEA) and extended with butylene glycol (BG) was synthesized via a two steps polymerization technique. The thermal stability of the PU was investigated by thermogravimetric analysis (TG) at temperatures between 30 and 600°C. The synthesized PU was irradiated in an UV exposure unit as such the spectral distribution of the light was a good match for terrestrial solar radiation (200 h, $\lambda > 300$ nm, Ia = 30 mW cm^{-2}). The modifications in the chemical structures of the PU before and after irradiation were characterized using Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR) technique. The yellowing index variation (YI) exhibited a systematic trend increase with irradiation time. Our results are in agreement with the formation of quinoide structures, which are colored products resulting from photo-degradation of PU.

Keywords: polyurethane, thermal analysis, photostability, thermal stability

At present, polyurethane coatings are the predominant types of topcoats used in the aircraft. Polyurethanes are also recommended for biomedical applications as adhesives, vascular and orthopedic protheses [1]. The coatings face outdoor exposure continuously throughout their service life. The stability of polymer coatings toward heat, moisture, oxidation and exposure to light is a topic of considerable complexity and of great practical interest [2-4]. Thermogravimetry (TG) is an efficient accelerated testing method that allows extrapolation of results obtained from high temperatures to low temperatures encountered in use [5]. TG analyses are useful when the coating temperature stability must be predicted. Traditional methods routinely used to examine weathered paints are physical techniques such as weight loss, color change and gloss loss [6]. Although they can be used to describe the level of coating degradation, they are not suitable for understanding why and how the coating degradation occurs and do not lead easily to lifetime prediction. In recent years, the significance of X-ray photoelectron spectroscopy and Fourier Transform infrared spectroscopy (FTIR) in polymer chemical analysis has been recognized [7, 8]. It was reported that photo-degradation occurs in polyurethanes (PUs) by forming hydro-peroxides in the presence of oxygen [9]. Saturated polyesters can react with oxygen to form carbonyl or peroxide groups through main chain scission. Thus, photo-initiated oxidation produces peroxides, ketones and aldehydes, and further photo-oxidation of peroxides and ketones yields peracids, which continue the oxidative degradation acting as oxidants [10].

The mechanism of photo-oxidative degradation of PU is known [1, 12]. Depolymerization, random chain scission and carbomethoxy side group abstraction are the main reactions after photon absorption. In air atmosphere, the formed free radicals react with oxygen giving hydroperoxides, which are photo-unstable and undergo further photochemical processes with formation of various oxidized products (containing different types of hydroxyl and carbonyl groups including ketones, aldehydes, esters, carboxylic acids). Moreover, the degraded chains become shorter and more mobile, fact which facilitates their rearrangements and local conformational changes [13]. For the application of PUs, their stability against terrestrial weathering is important. One of the greatest factors in the terrestrial weathering of PUs is the ultraviolet (UV) radiation in the wavelength range 330–410 nm. This energy, from incident energy solar radiation, initiates an auto oxidative degradation process in PUs that can chemically crosslink the chains extensively, embrittling and insolubilizing the PUs, particularly aromatic PUs [14]. Although the materials with urethane structure exhibit good mechanical properties [15], their use for surface coatings in outdoor applications is limited by the sensitivity to the photooxidative degradation [16].

In this study the thermal and photochemical stability of PU was investigated by means of TG measurements, FTIR-ATR spectroscopy, gloss retention variation and yellowness index. Our results are in agreement with the quinoide structure (yellow color) formation as the chromophoric reaction product during the photochemical degradation.

Experimental part

Synthesis of polyurethane

PU was synthesized using a copolyester poly (ethyleneadipate) diol (PEA) obtained by fusion condensation of adipic acid, ethylene glycol, diethylene glycol (1:0.5:0.6 molar ratio) with 4,4'-diphenyl-methanediisocyanate (MDI) (scheme 1). Reference [17] provides a detailed description of the copolyester synthesis.

The copolyester used for PU synthesis had a number-average molecular weight of 2000, and acidity index of 0.02 mg KOH g^{-1}.

The PU synthesis was performed as in reference [18]. The molar ratio of the components was PEA:MDI:BG = 1:6:5. Butylene glycol (BG) was used as a chain extender. The reaction was carried out in solution with dimethylformamide (DMF) as solvent during 4h. The reaction temperature was kept in the range of 75-80^{0}C. The number average molecular weight of the synthesized PU, determined from gel permeation chromatography (GPC), was $\overline{M}_n$=120.000.

Polymer films preparation

Films were prepared by casting the PU solutions in DMF on glass surfaces and allowing them to dry at room

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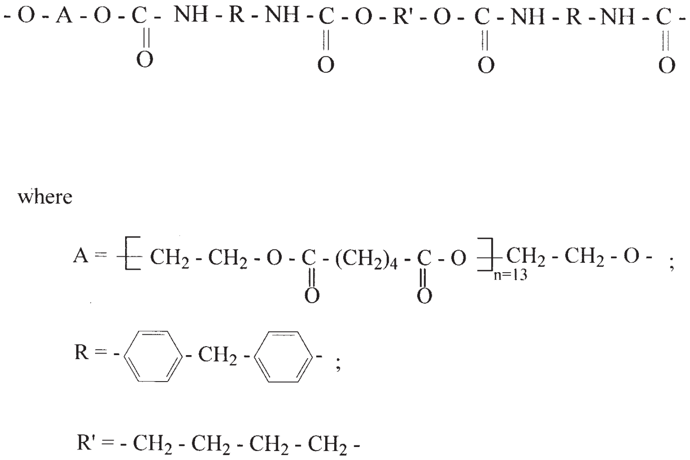


Scheme 1. The chemical structure of PU sample

temperature for 48h in the first stage, and then at 50^0C for another 48h. After demoulding, the films were kept into desiccators to avoid moisture uptake.

Thermogravimetric analysis

Thermogravimetric analysis was performed using a 449 FI Jupiter apparatus (NETZSCH-Germany). Samples of 7-8 mg as films were heated from 25 up to 600°C under a flow of N_2 (flow rate 50 mL/min) in an open Al_2O_3 crucible. The heating rates were chosen to be as 5, 10 and 20 K· min^{-1}. The kinetics parameters of PU thermal decomposition were calculated by Friedman method [19] with equation 1, where A, E and x are the pre-exponential factor, the activation energy and the degree of conversion, respectively.

$$\log\frac{dx}{dt} = \log A - \frac{E}{RT} - \log(1-x) \qquad (1)$$

The transformation of measured data into the degree of conversion x_i at the time i_t was calculated from thermograms according to the equation 2, where $m(t_s)$, $m(t_i)$ and $m(t_f)$ are the signals corresponding to the start time, a specified time, and the end time, respectively.

$$x_i = \frac{m(t_s) - m(t_i)}{m(t_s) - m(t_f)} \qquad (2)$$

Calculations were made using the Netzsch Thermokinetics 3 software.

UV exposure

The polyurethane samples were irradiated in air, in a rotative device equipped with a middle pressure mercury lamp HQE-40 type, having a polychrome emission spectrum in the domain of 240–570 nm, with a 30 mW/cm^2 light intensity. The more energetic radiations with $\lambda < 300$ nm, not presented in the natural light spectrum, were eliminated using a 30μm borosilicate glass filter. A water filter and a fan were used to prevent the thermal degradation of the sample during the photochemical treatment. The PU samples were placed on the device, which was positioned at a distance of 60 mm from the lamp. The temperature inside the irradiation chamber was kept around 40–45°C. The samples were withdrawn from the device at different photo-oxidative times ranging from 25 to 200h of exposure.

ATR-Fourier transform infrared spectroscopy (FTIR)

The ATR-FTIR spectra of the UV-cured films during the irradiation were obtained with a Bruker Vertex 70 spectrometer coupled with attenuated total reflectance equipment provided with a diamond crystal. All the spectra were acquired with a spectral resolution of 4 cm^{-1}.

Color measurement

The yellowness index of the PU specimens surface (YI) was measured with a color comparison spectrophotometer, Color QA^{TM}–PC Series model. The color comparison device was provided with a sensor head of 6 mm. The color analyses was done by comparing the color of the samples surface relative to a barium sulfate pills, regarded as absolutely white.

YI according to ASTM method E313 for 10^0 observer and D65 illuminant was calculated by following equation:

$$YI = \frac{100(1.3013\cdot X - 1.1498\cdot Z)}{Y} \qquad (3)$$

where X, Y and Z are the International Commission on Illumination (CIE) tristimulus values resulted from analysis.

Optical micrographs

Optical micrographs were obtained with the optical microscope MC5A having a power zoom of 300x.

Gloss measurement

The modification of the gloss at the samples surface during irradiation was monitored by means of the Gloss Chacker IG-320 apparatus.The gloss value was determined comparing the intensity of the sample luminous reflection with the value registered for a standard surface (polished black glass). The surface gloss retention (%) was calculated using equation (4):

$$\text{Gloss retention (\%)} = (G_f/G_i) \times 100 \qquad (4)$$

where G_i and G_f are the initial and current gloss values, respectively.

Results and discussion

Thermogravimetric study

TG and DTG curves recorded during the thermal decomposition of PU are shown in figure 1.

The thermograms presented in figure 1 shift to higher temperatures with increasing of the heating rate. DTG curves show at least four stages of thermal decomposition that are partially overlapped. Some data extracted from the thermograms such as the initial temperature of decomposition (T_i), the temperatures that correspond to 10% weight loss (T_{10}), 50% weight loss (T_{50}) and the final temperature (T_f) are given in table 1. The weight loss of PU sample at the end of thermal decomposition (W_f) is also given here.

PU thermal decomposition begins at temperatures higher than 200°C and completed over 560°C, as can be seen from figure 1 and table 1.

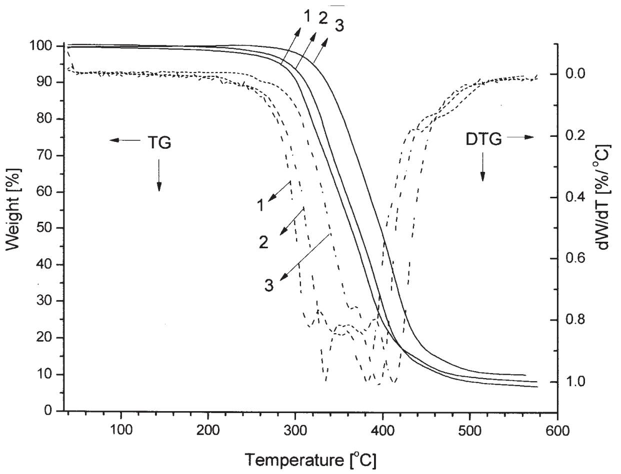


Fig.1. TG and DTG curves recorded during the thermal decomposition of PU at different heating rates: 5K min^{-1}; 10K min^{-1}; 20K min^{-1}

The graphical representation of log dx/dt as a function of 1/T in accordance with Friedman iso-conversion method is shown in figure 2.

Figure 2 confirms the thermal decomposition of PU in several stages. The kinetic parameters such as the activation energy (E) and the pre-exponential factor are presented in table 2.

The data from table 2 show the increase of activation energy with the conversion degree. It is an indication of a complex reaction mechanism.

Figure 3 presents the prediction of iso-conversional curves calculated with the aid of kinetic data versus the time and temperature.

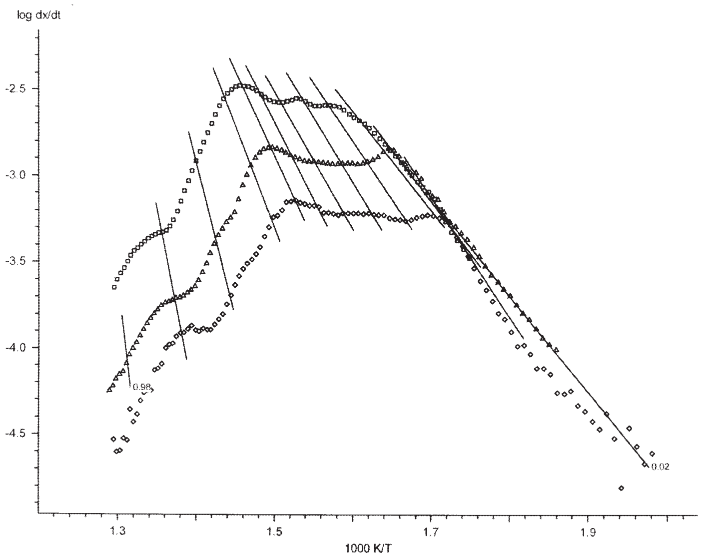


Fig.2.The graphical representation of log dx/dt as a function of 1/T in accordance with Friedman iso-conversion method

The data presented in figure 3 could be used to predict the lifetime of PU exposed to different temperatures.

Photochemical degradation study

The PU samples age during the exposure to polychromic light. The yellowness index increased with the exposure time as can be seen from figure 4.

The data from figure 4 show that the yellowness index almost tripled in the first 25 h of irradiation. This can be attributed to the massive accumulation of chromophores on the surface of sample. The extension of the irradiation time up to 200h induces a slowly increase of yellowing

Table 1
SOME DATA EVALUATED FROM THE THERMAL DECOMPOSITION CURVES

Heating rate K·min^{-1}	T_i (°C)	T_{10} (°C)	T_{50} (°C)	T_f (°C)	W_f (%)
5	210	302	364	577	91.6
10	242	312	373	577	92.9
20	244	337	398	564	89.8

Table 2
CHANGES IN KINETIC PARAMETERS OF THE PU THERMAL DECOMPOSITION REACTION WITH THE DEGREE OF CONVERSION

Degree of conversion	E kJ mol^{-1}	log A
0.05	131	8.58
0.10	114	7.06
0.20	110	6.66
0.30	129	8.17
0.40	144	9.22
0.50	153	9.79
0.60	172	11.22
0.70	188	12.34
0.80	224	14.96
0.90	342	23.00
0.98	719	46.90

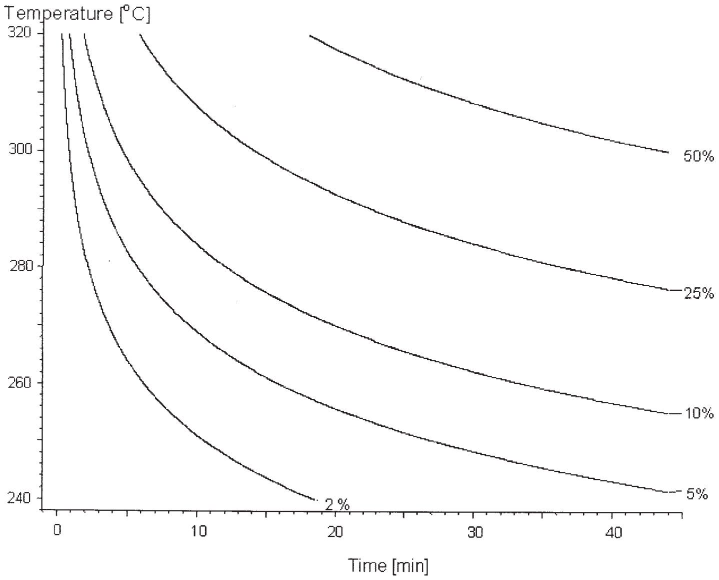


Fig. 3.Predictions of the iso-conversional curves of different weight loss during the thermal degradation of PU

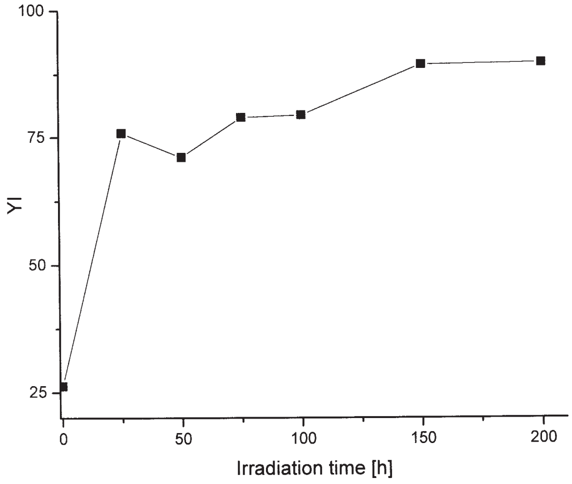


Fig.4.Variation of the yelowness index during the irradiation of PU sample

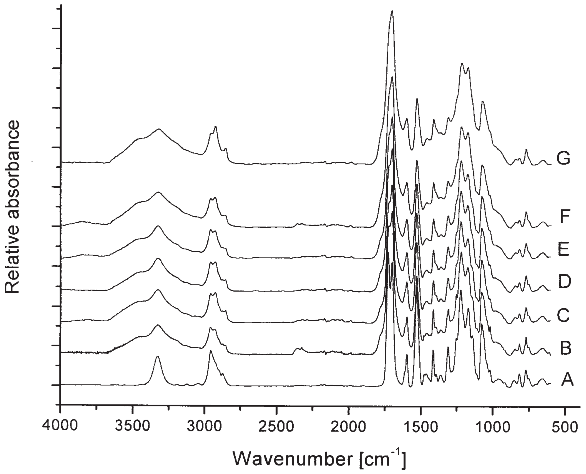
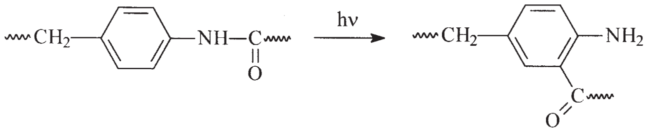


Fig. 5.FT-IR spectra of PU: non-irradiated sample (A), irradiated sample 25h (B), 50h (C), 75h (D), 100h (E), 150h (F) and 200h (G)



Scheme 2. Photo-Fries rearrangement of the urethane bond during the irradiation

index being an evidence of slowly accumulation of chromophores. The structural changes produced by the light on the PU sample were monitored by ATR-FTIR.

The changes in the FTIR spectra recorded for PU before and after irradiation are shown in figure 5.

The FTIR bands specific to non-irradiated PU sample are given in table 3 [20-22].

Significant changes in the FTIR spectrum of PU were observed after irradiation, as it is shown in fig. 6 where the difference between the FTIR spectrum of non-irradiated sample and the FTIR spectrum of PU recorded after 25h irradiation time is presented.

Table 3
FTIR CHARACTERISTIC BANDS OF PU

Wavenumber (cm^{-1})	Main assignment
3328	ν_{N-H}
2956 and 2870	ν_{CH_2}
1730	$\nu_{C=O}$ in ester
1705	$\nu_{C=O}$ in urethane chemical bond (amide I band)
1597	Skeletal C=C vibrations in aromatic ring
1531	Coupling of NH bending vibration with C-N stretching vibration in the C-NH group (amide II band)
1314	Amide III band
1300-1100	$\nu_{C=O}$ in ester
814	C-H bending vibration in 1,4 disubstituted aromatic ring

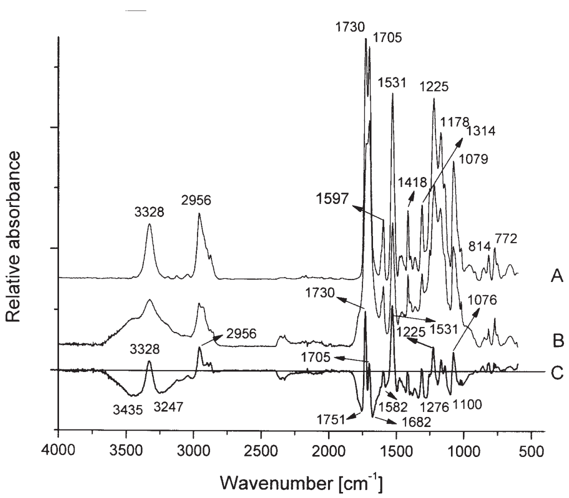
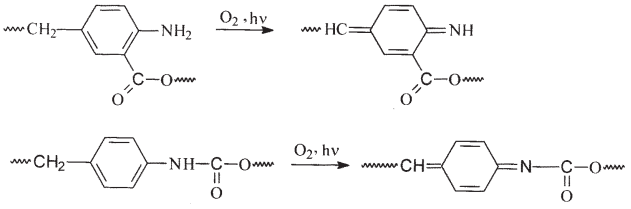
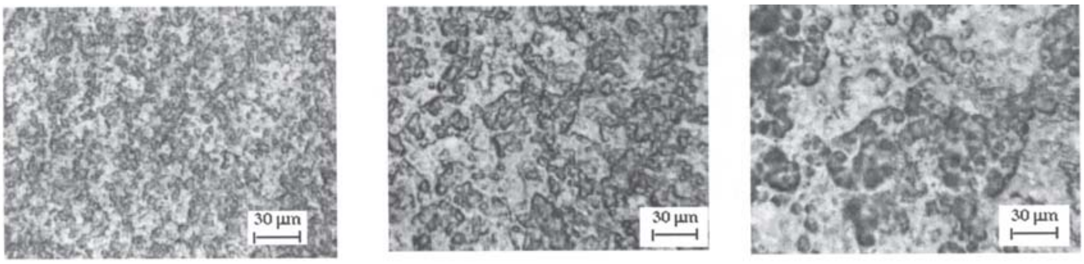


Fig.6.FTIR spectra of PU: (A) non-irradiated sample; (B) after 25h irradiation time; (C) difference between the spectrum (A) and the spectrum (B).



Scheme 3. The C=N structure appeared as a result of photo-oxidation of aromatic amines and/or of the hard segments from PU sample



(a) (b) (c)

Fig.7.Optical micrographs of PU sample: (a) non-irradiated sample; (b) after 100h irradiation time; (c) after 200h irradiation time.

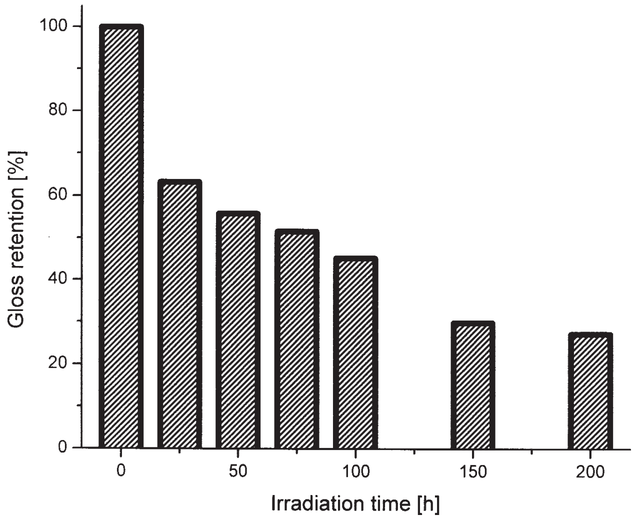


Fig.8.Variation of gloss retention with irradiation time

It can be observed from figure 6 that in the difference spectrum appeared some positive signals at 3328, 2956, 1730, 1705, 1225 and 1076 cm^{-1} and the negative intensities at 3435, 3247, 1751, 1682, 1582, 1276 and 1100 cm^{-1}. The positive absorbances reflect the chemical structures that disappeared during irradiation. Decrease of signals from 3328 cm^{-1} and 1705 cm^{-1} indicates the destruction of urethane bonds during the exposure of sample to the light. The new peaks from 3435 cm^{-1} and 3247 cm^{-1} are specific to the primary aromatic amines resulted after the photo-Fries rearrangement of hard segment in PU [23, 24]. Scheme 2 presents the photo-Fries rearrangement of the urethane bond during the irradiation.

The new signal from 1582 cm^{-1} appeared in the irradiated sample can be explained by the presence of C=N vibrations. The C=N structure appeared as a result of photo-oxidation of aromatic amines and/or the hard segments from PU sample is shown in scheme 3.

The accumulation of photo-oxidation compounds with quinoide structure (1) and (2) explains the color changes of PU samples during irradiation.

The aliphatic ester structure from the PU sample is also sensitive to the light. The decrease of signals from 1730 cm^{-1} and 1225 cm^{-1} proves this observation. The new peak from 1751 cm^{-1} is an indication of the formation of some oxidation products with peroxide structure during irradiation.

Saturated ester structure from PU sample undergoes some photo-decomposition reactions of Norrish type accompanied by release of carbon dioxide [25]. Such reactions lead to increase of roughness of polymer film during the light exposure. Changes in the roughness of PU samples during irradiation have been revealed by optical microscopy, as shown in figure 7.

From figure 7 results the increase of roughness of PU sample with irradiation time. The PU surface becomes much wrinkled of bubbles and rougher after 100h and 200h of irradiation time than that of non-irradiated sample. A consequence of roughness increase is decreasing of gloss. Figure 8 presents the gloss retention variation with irradiation time.

Figure 8 shows a significant loss of gloss during exposure of PU samples to the light. In the first 25 h of exposure to the polychromic light, the gloss of samples decreased with 36.7% while the total decrease of gloss after 200h irradiation time was 72.9%.

Conclusions

The thermal stability of aromatic polyurethane based MDI was investigated by thermogravimetry at three different heating rates (5, 10 and 20 K·min^{-1}). The polyurethane is stable in inert atmosphere at temperatures up to 210°C. Thermal decomposition of polyurethane occurs in several stages between 210-580°C. The activation energies and the pre-exponential factors increase with the conversion degree indicating a complex mechanism of thermal degradation. Based on the kinetic parameters, the isoconversional curves of different weight loss values were calculated.

Photochemical stability of PU sample was investigated by irradiation with polychromic light having $\lambda > 300$ nm. Significant changes of yellowness index and gloss were identified in the first 25h irradiation time. Accumulation of some photo-degradation compounds with chromophore properties and the increase of surface roughness were identified during the exposure to light of the polyurethane sample.

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