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Infrared study of the photochemical behaviour of aromatic Poly (ether urethanes)

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Abstract: Poly(ether urethanes) based on aromatic diisocyanates and poly(propylene glycol) of different molecular weight and different hard segment content have been synthesised. The extent of the photooxidation of UV exposed samples has been evaluated by FTIR spectroscopy. The results proved that both the isocyanate chemical nature and polyol molecular weight play an important role in the photooxidation behaviour of these systems.

Keywords: Aromatic poly(ether urethanes); photooxidation; FTIR.

Introduction

It is well known that aromatic segmented polyurethanes rapidly degrade and undergo yellowing on exposure to UV light [1, 2]. So the more expensive aliphatic polyurethanes often replace them.

It is well established that in 4,4'methylene bis(4-phenyl isocyanate) (MDI) based polyurethanes, the photochemical evolution of the aromatic moieties involves a dual mechanism. One is the photo-Fries type reaction [3] and the other is an induced oxidation of the central methylene group of MDI [4-6]. In toluene diisocyanate (TDI) based polyurethanes the induced oxidation cannot take place, so it can be argued that they are more stable than MDI based systems. Nevertheless, there are few studies [3] that compare the behaviour of these isocyanates.

However, commercial polyurethanes are block copolymers, which consist of polyol sequences (soft segment) and urethane sequences (hard segment). Polyol sequences play an important role in the photooxidation extent of the urethane hard segments. The radical species formed by the oxidation of soft segments can induce the oxidation of the aromatic urethane segments [7, 8].

Moreover, numerous studies have shown that the extension of the photooxidation is directly dependent on the flexibility of the polymer backbone. The photooxidation process is accelerated at temperatures above the glass transition temperature of the system, indicating the role of chain flexibility and/or oxygen diffusion in the decomposition process [9, 10].

The effect of polyol segment molecular weight and the concentration of urethane groups have also been extensively studied. According to different authors [11-13] the photooxidation is more prevalent in elastomers with lower hard segment concentration and with higher soft segment molecular weight.

In a previous work [14] we studied the photochemical behaviour of segmented aromatic polyether urethanes based on poly(tetramethylene oxide) trying to elucidate the role of the compatibility of hard/soft segments in the photochemical behaviour. In the present paper we will extend the study to other ether soft segment: poly(propylene glycol). Our efforts concentrate on obtaining evidences that will allow us to confirm the role of the system flexibility in the photooxidative behaviour.

Results and discussion

MDI based segmented polyurethanes

The infrared spectra of MP2.28 and MP4.64, at different UV exposition times, are shown in Figs. 1 and 2, and their infrared characteristic frequencies [16] are summarized in Table 1.

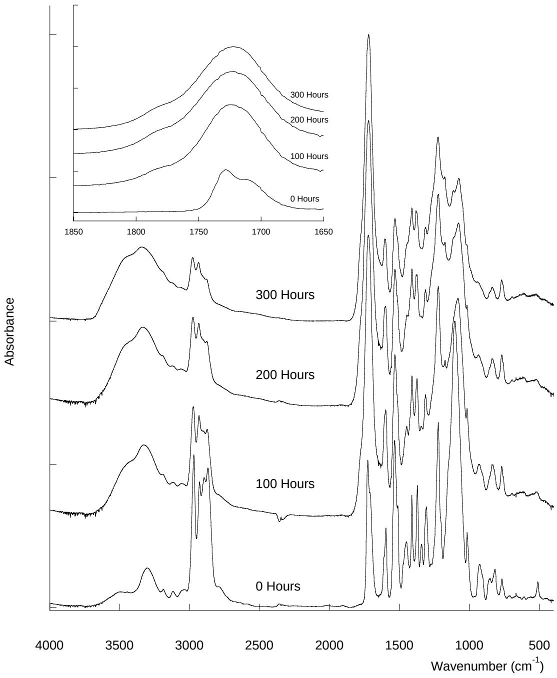


Fig. 1. FTir spectra of MPG2.28 at different irradiation times.

As can be seen in both figures, the UV radiation provokes chemical changes, which are reflected in the infrared spectra. These changes are more evident in the sample with higher soft segment content and molecular weight (MP2.28).

In order to perform a detailed analysis, the modifications of the infrared spectra can be separated in those concerning the polyether component and those of the urethane groups. Thus, if we focus our attention on the more relevant urethane group absorption bands we clearly observe a broadening of the NH stretching vibration band towards higher wavenumbers in such a way that it resembles an OH stretching vibration band. This modification is more evident in the system containing a higher molecular weight polyol and a lower hard segment percentage.

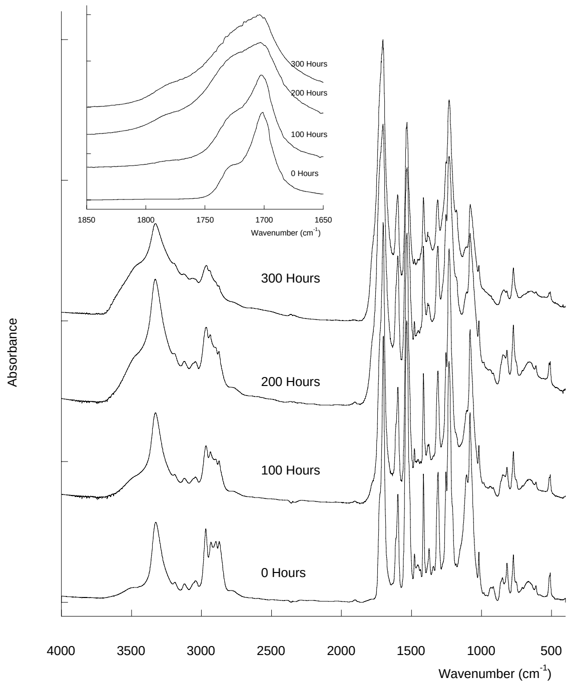


Fig. 2. FTir spectra of MPG4.64 before and after irradiation.

Tab. 1. Infrared characteristic frequencies of aromatic Polyurethanes.

Frequency (cm^{-1})	Relative intensity^{a}	Main assignments^{b}
3420	vw,sh	ν(N-H) free
3320	m	ν(N-H) associated
3050	w	Overtone of Amide II
1730	vs	ν (C=O) free
1707	vs	ν(C=O) associated
1600	m	ν(C=C) in aromatic ring
1533	vs	ν(C-N) + δ (N-H) (Amide II)
1475	m	δ CH$_2$
1263	s	ν(C-N)+ ν(C-O) (Amide IV)
1110	s	ν(C-O-C) in ether
816	w	δ oop =C-H in MDI and TDI
773	w	δ oop in COO urethane
638	w	ω (N-H) (Amide V)
612	vw	δ ip p-ring
513	vw	δ oop p-ring
455	vw	δ oop 1,2,4 ring

In addition, the so-called amide II band (1533 cm^{-1}) decreases in intensity as a function of the exposition time. These observations are perfectly in accordance with previous results [14] obtained for MDI based non-segmented polyurethanes, which supports the photooxidation mechanism proposed in literature. Concerning the ether group band, we notice almost a disappearance of the methylene and methyl asymmetric and symmetric stretching vibration bands. In addition, a reduction of the intensity of the band at 1100 cm^{-1} (ν C-O-C) can be observed, which strongly suggests the rupture of the ether linkage, accompanied with the evolution of volatile polyol segments, as a result of the exposure to the UV radiation.

In addition, a broadening of the urethane C=O stretching vibration band can be observed, as a consequence of the generation of new carbonyl moieties coming from photo Fries reaction as well as polyether oxidation. It is well known that through photo Fries reaction [17-19], urethane bonds are broken with the generation of new functional ester and amine groups together with an increased substitution of the aromatic ring. This is in full agreement with the observation of the modification of the corresponding aromatic out of plane bending vibrations. Thus, a decrease in the intensity of the band at 818 cm^{-1} (aromatic out of plane C-H deformation vibration in para disubstituted benzene) and the appearance of a band with a maximum at 840 cm^{-1} (aromatic out of plane C-H deformation vibration in 1,2,4-trisubstituted benzene) can be observed.

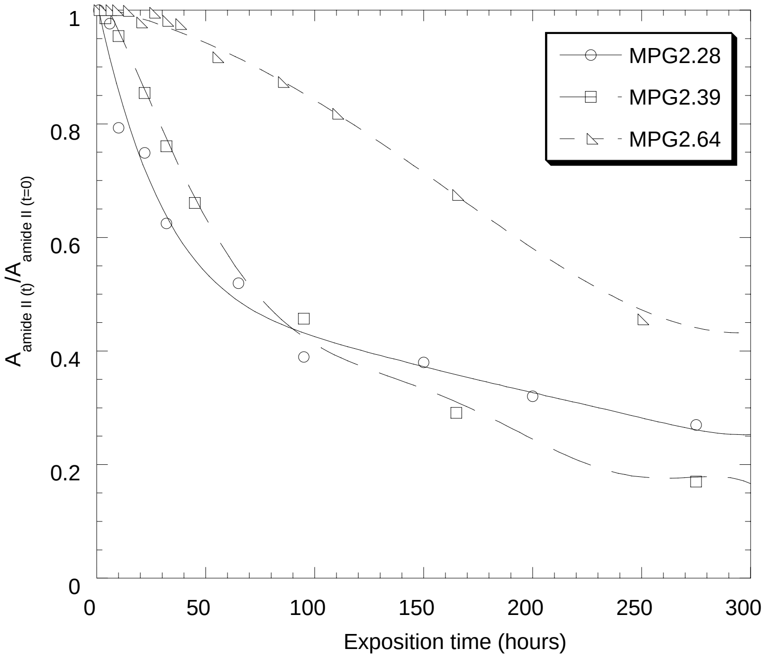


Fig. 3. Variation of normalised amide II band for MDI and PPG 2000 based samples as a function of the irradiation time.

In order to quantify the degradation of the urethane hard segments, the amide II band has been selected, because the C=O stretching vibration region has also contribution of the soft segment degradation. We have calculated the area of the amide II band at different exposition times and normalised to the value of the corresponding area of the non-exposed samples. The results of this calculation for the MDI and PPG 2000 based samples are shown in Fig.3.

If we compare the decrease of the amide II band for the three samples, we notice that the system with the higher hard segment percentage (MPG2.64) suffers the lower decrease along the whole period of time studied. On the contrary, the decrease in the other two samples can be considered quite similar, showing a higher decrease at short exposition times, and then a slow down. Taking into account that the hard segment content of these two samples is not very different, we can conclude that the presence of high molecular weight polyol promotes or induces the rupture of urethane bonds. Thus, the modification in the urethane hard segments increases as the soft segment concentration increases. Similar results have been obtained for lower molecular weight PPG based systems.

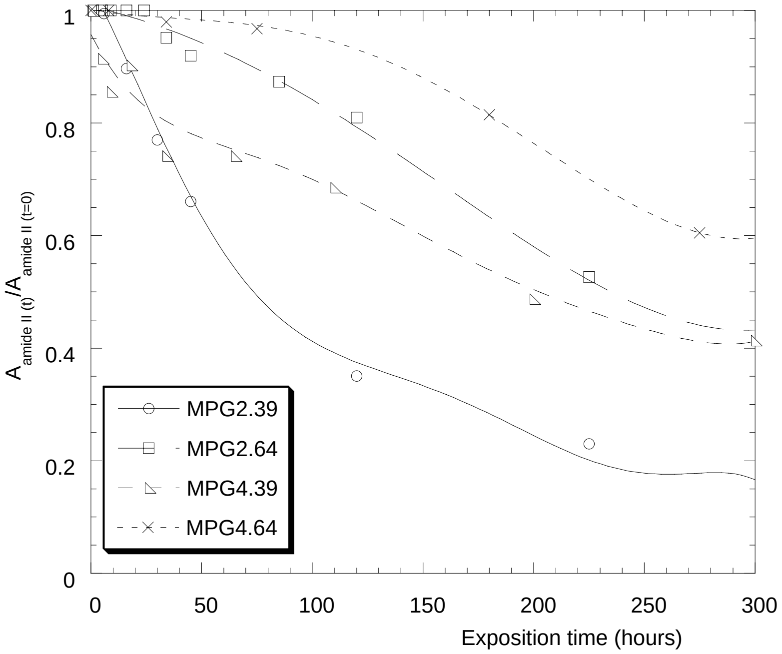


Fig. 4. Normalised decrease of the amide II band for indicated samples as a function of the irradiation time.

Fig. 4 shows the amide II band evolution for other systems. Comparing the amide II band evolution for samples having the same hard segment content; the higher polyol molecular weight, the higher the decrease of this band. The decrease of the amide II band in MDI based polyurethanes accounts for a dual mechanism: C-N bond photolysis (photo-Fries) and oxidation of the central methylene carbon group. It can be assumed that radical species formed by the oxidation of the polyether segments induce the oxidation of the central methylene group leading to the formation of quinone-imides. This hypothesis can satisfactorily explain that as the polyether content increases, the urethane degradation also increases. Nevertheless, this assumption is not valid to explain why the urethane group cleavage is more prevalent in samples with a higher soft segment molecular weight. As it has been reported in literature [14, 20], the higher photoresistance shown by low molecular weight soft segment systems is due to a higher interaction degree between hard and soft phases, as a consequence of a different distribution of the hard segments along the polyurethane chains. Moreover, this fact is responsible for the different physical properties shown by segmented polyurethanes of different soft segment molecular weight, which obviously interferes in the mobility of the polymer radicals and in the oxygen diffusion along the samples.

Tab. 2. Thermal transition temperatures for the studied polymers.

Sample	% HS	Soft segment molecular weight	T_{gs} (ºC)
MPG2.28	28	2000	-41
MPG2.39	39	2000	-39
MPG2.64	64	2000	-43
MPG4.39	39	425	17
MPG4.64	64	425	59
TPG2.28	28	2000	-51
TPG2.39	39	2000	-45
TPG2.64	64	2000	-49
TPG4.39	39	425	13
TPG4.64	64	425	47
PPG	0	425/2000	-70

Different studies have shown that the flexibility of the polymer chain has a direct effect on the photooxidation of the systems. The photo-Fries rearrangement ratio increases when the weathering temperature is above the glass transition of the polymer matrix [9]. According to this, the glass transition temperature of the samples must be an important factor to take into consideration in the study of the photooxidation of segmented Polyurethanes. Table 2 displays the soft segment glass transition temperatures for all the samples. As can be seen, the soft segment glass transition temperature for the systems based in 2000 molecular weight soft segment is lower than for systems based in 425 molecular weight. We can, thus, argue that the higher photoresistance showed by the low molecular weight based samples can be related with the lower flexibility of the samples.

TDI based segmented polyurethanes

The infrared spectra of TPG2.28 before and after irradiation are shown in Fig 5. As in MDI based polyurethanes, a loss of urethane and ether groups as a consequence of the exposition to the UV radiation is observed.

Figure 6 depicts the decrease of the amide II band for 2000 molecular weight based polyurethanes.

Here again, the higher soft segment percent the higher the rupture of the urethane linkage. The induced oxidation of methylene groups by the soft segment radicals cannot explain this phenomenon because the abstraction of a hydrogen atom is not possible in this case. Therefore, it can only be due to a different extension of photo-Fries reactions, which according to Hoyle et al. [9], depend directly on chain mobility.

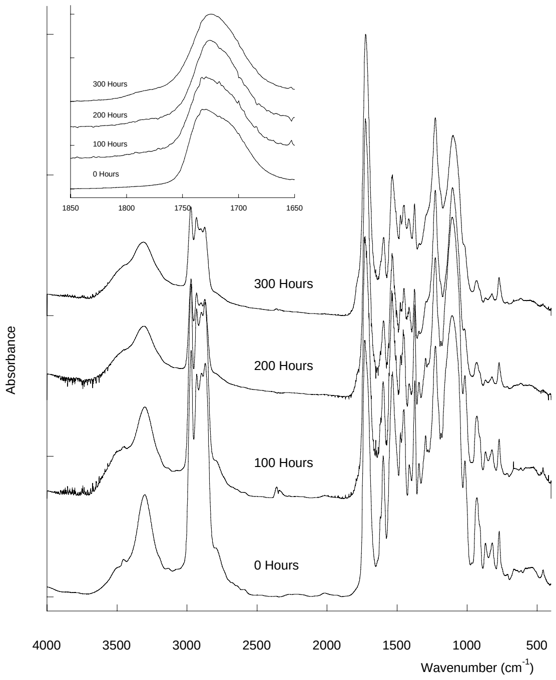


Fig. 5. FTir spectra of TPG2.28 before and after irradiation.

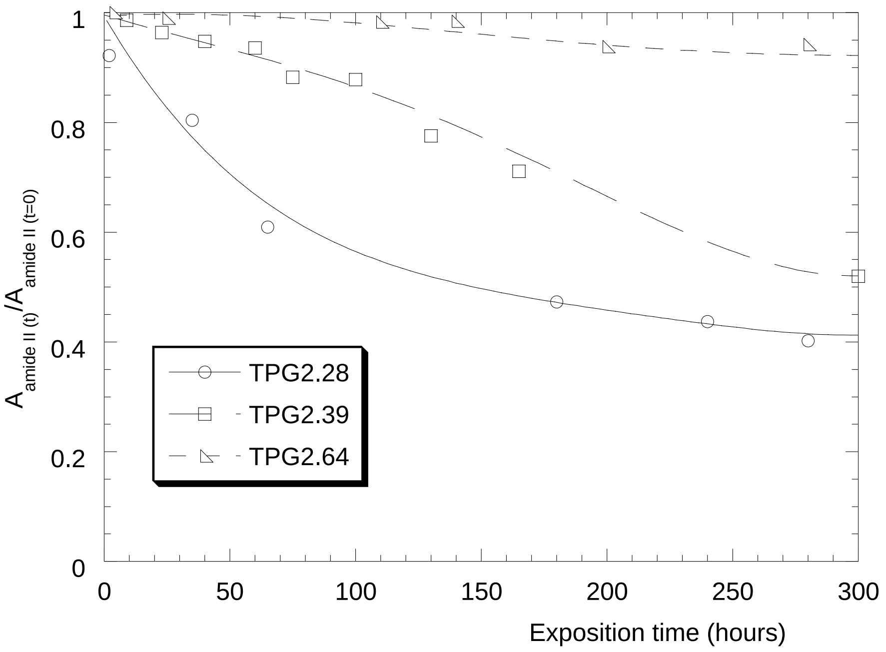


Fig. 6. Normalised decrease of the amide II band for TDI and PPG 2000 based samples as a function of the irradiation time

The results for the PPG425 based polyurethanes, are shown in Figure 7. As can be observed, the systems with the higher hard segment concentration do not achieve signs of degradation, irrespective of the soft segment molecular weight. However, for the systems with 39% of hard segment, the degradation rate increases with the molecular weight of the soft segment.

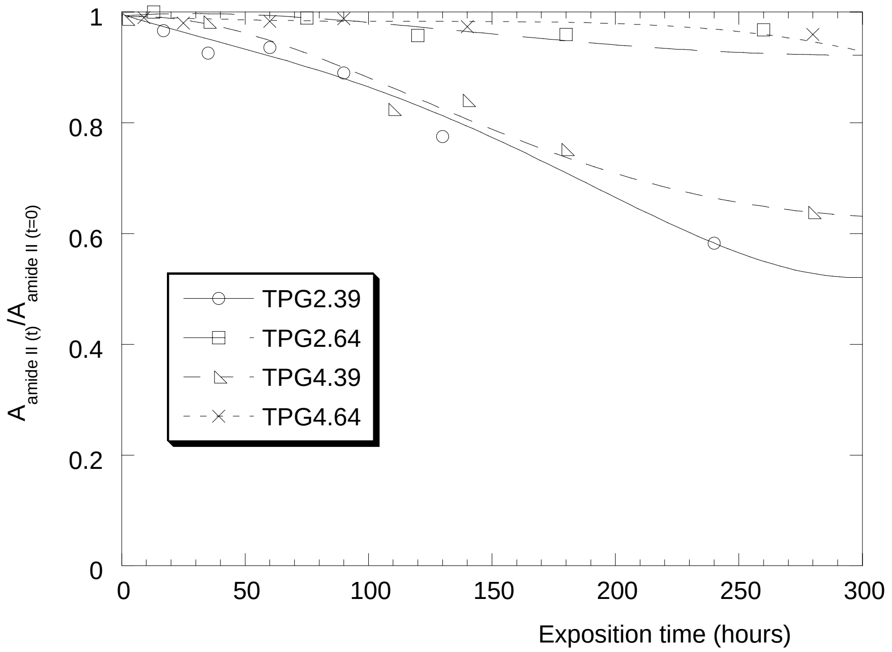


Fig. 7. Normalised decrease of the amide II band for TDI and PPG 425 based samples as a function of the irradiation time.

Comparing the extension of the degradation for TDI and MDI based polyurethanes, MDI based systems show a higher susceptibility to photooxidation than those based on TDI. It is clear that the presence of central methylene group in MDI play a key role on photooxidation behaviour.

Conclusions

The photooxidation behaviour of the studied segmented polyurethanes depends on flexible segment concentration. Thus, the systems with the higher soft segment content show the higher degradation extent. The lower chain mobility shown by the low molecular weight soft segment based polyurethanes accounts for the higher stability of these systems.

In addition, independent of hard segment concentration, the chemical nature of isocyanate is mainly responsible of the photooxidative behaviour of these systems. Thus, the MDI based polyurethanes show a higher susceptibility to photooxidation than those based on TDI isocyanate. It is clear that the presence of central methylene group in MDI play a key role on photooxidation behaviour.

Experimental

Materials

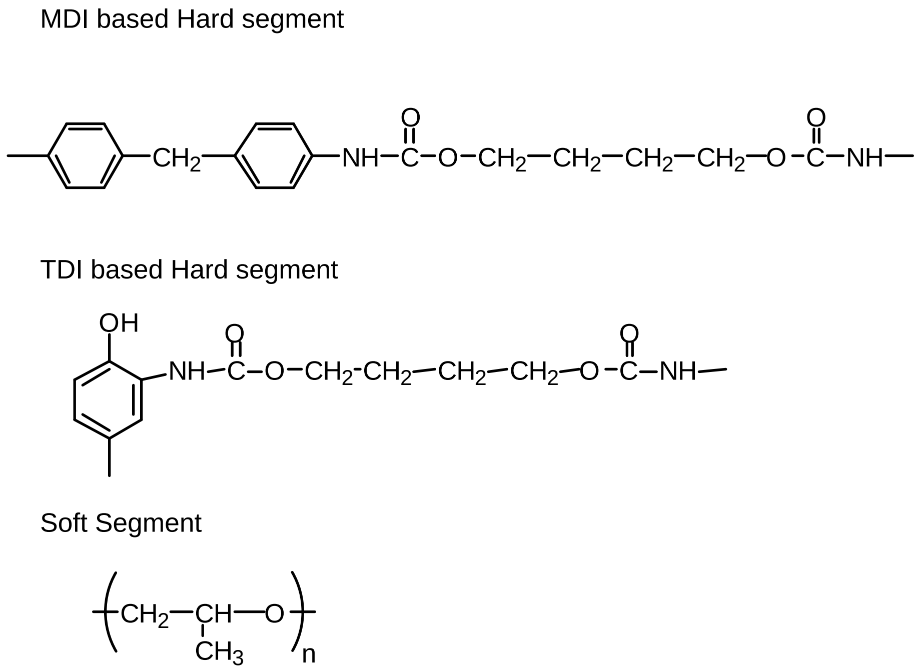
4,4’ Methylene bis(4-phenylisocyanate) (MDI) and 2,4-toluene diisocyanate (TDI) (Aldrich), mixture 80/20 of isomers 2,4 and 2,6 were distilled under reduced pressure. Poly(propylene glycol) (Aldrich) M_w=425 and M_w=2000 (PPG425,PPG2000) was degassed under vacuum at 50ºC overnight.

1,4-Butanediol (BD) (Aldrich) was distilled under vacuum and then stored over activated 4A type molecular sieves. N,N’ dimethyl formamide (DMF) was distilled under vacuum then stored over activated 4A type molecular sieves. Stannous octoate was purchased from Sigma, and used as received.

Polymerizations

Segmented polyurethanes were synthesised by the catalysed prepolymer technique in DMF solution [14, 15]. The polymerization reaction was carried out in a pyrex glass ampoule exhaustively flamed under high vacuum. The ampoules were equipped with a glass-teflon stopcock to facilitate the addition of the reactants under high vacuum conditions. PPG was placed in the ampoule. Appropriate amounts of diisocyanate (MDI or TDI) in sufficient anhydrous DMF to make 50% w/w solutions and stannous octoate (0.01% of total solids), were added to the flask. The mixture was heated to end-cap the macrodiol. The end-capping reaction was carried out for two hours at 60ºC for MDI based polyurethanes and for two hours at 25ºC for TDI based polyurethanes. The prepolymer was diluted to 25% (w/v) with anhydrous DMF and BD as a 10% solution in DMF was added with stirring under nitrogen atmosphere. The chain extension was carried out for 4 hours at 80ºC in all the studied polymers. The polymer was isolated by dropwise addition of the diluted polymer solution to 10 times its volume of deionized water with stirring. The precipitated polymer was filtered and thoroughly washed with water. A description of the obtained polymers is summarised in Table 3 and the chemical structures are described in Scheme 1. Hard segment concentration is defined according to equation 1.

$$\%\ Hard\ \ Segment\ (\%\ H.S.) = \frac{Weight_{diisocyanate} + weight_{BD}}{Total_{weight}} \qquad (1)$$



MDI based Hard segment

TDI based Hard segment

Soft Segment

Scheme 1. Structures of the studied systems.

Tab. 3. Description and nomenclature of synthesised polymers.

Isocyanate	Chain extender	Soft segment	% Hard segment	Nomenclature
MDI	BD	PPG2000	28	MPG2.28
MDI	BD	PPG2000	39	MPG2.39
MDI	BD	PPG2000	64	MPG2.64
MDI	BD	PPG425	39	MPG4.39
MDI	BD	PPG425	64	MPG4.64
TDI	BD	PPG2000	28	TPG2.28
TDI	BD	PPG2000	39	TPG2.39
TDI	BD	PPG2000	64	TPG2.64
TDI	BD	PPG425	39	TPG4.39
TDI	BD	PPG425	64	TPG4.64

Irradiation and analysis

An accelerated weathering device equipped with a xenon arc light source and a 300 nm filter was used. The average temperature measured in a black panel thermometer was 45ºC over the sample. Polymer samples were exposed to UV radiation during 300 hours and spectroscopically analysed at different intervals of time.

Polymer samples for infrared study were prepared by casting films on KBr windows. After most of the solvent had evaporated, the samples were carefully dried under vacuum at 50 ºC for 72 hours to completely remove residual solvent. Sample thickness was controlled by the regulation of the initial absorbance on the carbonyl stretching vibration to 1, in order to fulfil Lambert Beer law. This means that the sample film thickness is thinner than 10μm.

Infrared measurements were recorded on a Nicolet model Magna 560, FTIR spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 runs were signal averaged.

DSC studies were carried out in a Perkin Elmer calorimeter, model Pyris 1. The heating rate used was 20ºC min^{-1} over a temperature range from -70 to 140ºC under nitrogen atmosphere. The sample weight was approximately 10 mg. Internal calibration was carried out with dodecane and indium.

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