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Aromatic poly(ether-urethanes): effect of the polyol molecular weight on the photochemical behaviour

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Abstract

Poly(ether-urethanes) based on 4,4′-methylene bis (4-phenylisocyanate) or toluene diisocyanate and poly(tetramethylene oxide) have been synthesised varying the molecular weight of the soft segment. The hard/soft segment mixing has been studied by differential scanning calorimetry and Fourier transform infrared spectroscopy. The polymers have been exposed to UV radiation, and the changes in the chemical structure have been analysed by FTir spectroscopy. The extent of the photodegradation in the urethane linkage increases with soft segment molecular weight. The phase separated structure is a critical factor which must be taken into account in order to study the photodegradation of the hard segments in poly(ether-urethanes). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Aromatic poly(ether-urethanes); Photodegradation

1. Introduction

Segmented polyurethanes present unusual properties directly related to their two phase microstructure [1,2]. This microstructure is a consequence of the thermodynamic incompatibility between the hard and the soft segments. Both the perfection and degree of phase separation play an important role in the strength and high elasticity of the final polymers. It appears that the degree of microphase separation determines the relative amount of the two main types of hydrogen bonds observed in polyether and polyester urethanes. Due to this fact, many studies have been devoted to direct measurements of the extent and nature of hydrogen bonding in polyurethanes by infrared spectroscopy [3–5].

Despite the wide properties displayed by these materials, a major limitation relates to their use as surface coatings in outdoor applications. In these outdoor applications, photo-oxidation behaviour of these materials is a determining factor which can lead to the failure of an excellent mechanical properties formulation.

Photolysis of aromatic diisocyanate based polyurethanes has been studied by Gardette and Lemaire [6] considering the effect of the excitation wavelength. At short wavelengths (< 340 nm) photolysis of the C–N bond takes place giving rise to macroradicals. The major route of evolution of these radicals is the Photo-Fries type rearrangement. This reaction is responsible for the yellowing of aromatic diisocyanate based polyurethanes under non-oxidative conditions. However, some of the radicals can escape from the cage reaction leading to the formation of aromatic amines.

In the presence of oxygen, oxidation of urethane segments occurs in MDI based polyurethanes. This reaction involves a radical attack on the central methylene carbon of the aromatic structures with the subsequent formation of hydroperoxides. These groups will lead to quinone-diimide structures as well as benzoic acid end-groups [7].

It is well known that in the induced photo-oxidation of polyethers, hydroperoxy radicals are formed in the carbon in α position to the ether oxygen atom. In this sense, Gauvin and Lemaire [8] have proposed that the fundamental photo-oxidation reaction that gives poly(tetramethylene oxide) is the β scission, leading to the formation of formate groups.

The effect of the physical state on the photolysis of polyurethane elastomers has been investigated by different authors [9]. Thus, Frish et al. [10], in their researches on aromatic polyurethanes, conclude that the resistance to photodegradation is enhanced by both the increase of hard segment concentration and the decrease of soft segment molecular weight.

Hoyle et al. [11], working with the same type of systems, have proposed that the extent of the photolysis reaction is inversely dependent on the degree of hydrogen bonding in aryl carbamate groups present in the polyurethane backbone.

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Table 1
Description and nomenclature of synthesised polymers

Isocyanate	Chain extender	Soft segment	% Hard segment	Nomenclature
MDI	BD	/	100	MDIBD
TDI	BD	/	100	TDIBD
MDI	BD	PTMO650	54	MT6.54
MDI	BD	PTMO650	28	MT6.28
MDI	BD	PTMO2000	28	MT2.28
TDI	BD	PTMO650	47	TT6.47
TDI	BD	PTMO650	22	TT6.22
TDI	BD	PTMO2000	22	TT2.22

The aim of the present study is to establish the photodegradation susceptibility of different molecular weight soft segment poly(ether-urethanes) based on aromatic diisocyanates, and to try to elucidate the role of the compatibility of hard/soft segments in the observed photodegradation behaviour.

We have studied the compatibility between hard and soft segments by differential scanning calorimetry (DSC) and by Fourier transform infrared spectroscopy (FTir). The polymers have been irradiated in an artificial weathering device equipped with a xenon arc lamp. Changes in the polymer structure provoked by the UV radiation have been monitored by FTir spectroscopy and samples weight loss have been measured.

2. Experimental

2.1. Materials

4,4′ methylene bis (4-phenylisocyanate) (MDI) (Aldrich) was distilled under reduced pressure.

2,4-toluene diisocyanate (TDI) (Aldrich), mixture 80/20 of isomers 2,4 and 2,6 was distilled under reduced pressure.

Poly(tetramethylene oxide) (Aldrich) of $M_w = 650$ and $M_w = 2000$ (PTMO650, PTMO2000) was degassed under vacuum at 50°C overnight. The average molecular weight was calculated using ^{1}H-NMR.

N,N′-dimethyl formamide was distilled under vacuum to avoid thermal decomposition, and stored over activated 4 Å type molecular sieves.

1,4-butanediol (BD) (Aldrich) was distilled under vacuum and then stored over activated 4 Å type molecular sieves.

Stannous octoate (Sigma) was used as received.

2.2. Polymerisation

Linear polyurethanes obtained from 1,4-butanediol and MDI or TDI were synthesised by solution polymerisation [12].

Segmented polyurethanes were synthesised by a prepolymer technique [13] under the following procedure.

The polymerisation 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.

The macrodiol was placed in the ampoule. Appropriate amounts of diisocyanate (MDI or TDI) in sufficient anhydrous dimethylformamide 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 60°C for MDI based polyurethanes and for two hours at 25°C for TDI based polyurethanes.

The prepolymer was diluted to 25% (w/v) with anhydrous dimethyl formamide. The chain extender (1,4-butanediol) was then added with stirring under nitrogen atmosphere as a 10% solution in dimethyl formamide. The chain extension was carried out for 4 h at 80°C in all the obtained 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 1.

2.3. Irradiation and analysis

The polymer samples were irradiated in an accelerated weathering device equipped with a xenon arc light source. The more energetic radiation (not present in natural weathering), was eliminated using a 300 nm borosilicate filter. The temperature inside the irradiation chamber was kept constant using a ventilator. The average temperature measured in a black panel thermometer was 45°C over the sample.

The samples to be irradiated were prepared by casting in anhydrous dimethyl formamide over potassium bromide windows. The samples were dried under vacuum, initially at room temperature and afterwards at 60°C. Sample thickness was controlled by the regulation of the absorbance of the carbonyl stretching vibration to 1.0.

In order to ensure that chemical evolution is the result of UV irradiation and not film thickness, only one sample was used for each formulation.

Polymer samples were exposed for varying time intervals and then analysed spectroscopically.

Table 2
Thermal transition temperatures for the studied polymers

Polymer	% Hard segment	Soft segment molecular weight	Thermal transitions (°C)
PTM0650	0	650	T_g (onset) = − 89 T_m (max) = 18
PTMO2000	0	2000	T_g (onset) = − 93 T_m (max) = 22
MDIBD	100	–	T_g (onset) = 99 T_m (max) = 222
TDIBD	100	–	T_g (onset) = 99
MT2.28	28	2000	T_g (onset) = − 72
MT6.28	28	650	T_g (onset) = − 43
MT6.54	54	650	T_g (onset) = 11 T_m (max) = 148
TT6.47	47	650	T_g (onset) = − 19
TT2.22	22	2000	T_g (onset) = − 76 T_m (max) = 19

FTir spectra were recorded using a Nicolet 5DXC spectrometer equipped with a DTGS detector. The spectra were obtained at a resolution of 2 cm^{-1} using 64 scans summation.

DSC studies were carried out in a Perkin Elmer DSC-2. The heating rate used was 20°C min^{-1} over a temperature range from − 120°C to 240°C in a nitrogen atmosphere. The sample weight was approximately 10 mg. Internal calibration was done with dodecane and indium.

The films used for weight loss measurements were prepared by casting over Petri dishes. The samples were weighted at different irradiation times.

3. Results and discussion

3.1. DSC studies

The values of thermal transitions obtained for the studied polymers are summarised in Table 2.

Polytetramethylene oxide has a glass transition temperature of − 90°C, and no effect of the molecular weight was observed. The two polytetramethylene oxide samples also present a melting endotherm. The melting point is higher for the system with a higher molecular weight. Non-segmented polyurethanes based on MDI and TDI show the same T_g value; however, only that based on MDI shows an endothermic peak at 222°C. Due to the asymmetric structure of 2,4-TDI, only amorphous structures are formed in this system.

DSC spectra of segmented poly(ether-urethanes) display T_g values in a wide temperature range, depending on soft segment molecular weight, diisocyanate chemical structure and hard segment concentration. As stated before, in segmented polyurethanes phase separation takes place due to thermodynamic incompatibility between soft and hard segments. Therefore, changes in the glass transition temperature of the soft segment (T_{gs}) can be used as a measure of the soft/hard phase mixing. A T_{gs} nearly the same as that obtained for pure poly(tetramethylene oxide) (soft segment), reflects very low phase mixing, whereas an increase in T_{gs} reflects higher phase mixing.

In all the segmented polyurethanes studied, an increase in the soft segment glass transition temperature (T_{gs}) is observed when compared with the obtained for pure poly(-tetramethylene oxide), indicating some extent of soft/hard phase mixing. This increase is due, in part, to a decreased mobility of the soft segments because of their attachment to stiffer groups. Penetration of isolated hard segment units into the soft segment phase also contributes to the effect on T_{gs}.

Three factors must be taken into account to analyse the obtained values of T_{gs}: Hard segment concentration, soft segment molecular weight and chemical nature of the hard segment.

Thus, those polyurethanes having a soft segment molecular weight of 2000, show a fairly similar soft segment T_{gs} at about − 75°C, regardless the chemical nature of the diisocyanate. These T_{gs} values are close to the observed value for pure PTMO, indicating a very low phase mixing.

However, those samples based on 650 soft segment molecular weight differ on behaviour regarding both the chemical nature of the diisocyanate (MDI or TDI) and the hard segment concentration. The observed values are, in all cases, higher than the corresponding value of PTMO. In addition, the T_{gs} value increases as the hard segment concentration increases. This can be attributed to a combination of the copolymer effect and effective crosslinking of soft block oxygens by hydrogen bonding with urethane N–H groups.

In order to study the effect of the chemical nature of the hard segment (MDI or TDI), we can compare the results obtained for the samples constituted by soft segments of equal molecular weight, similar hard segment concentration and different chemical nature of the hard segment. As can be seen in Table 2, T_{gs} is higher in MDI based polyurethanes, reflecting more phase mixing. This behaviour is surprising as hard segments in MDI based polyurethanes can crystallise while hard segments in TDI based polyurethanes can not. The crystallisation of the hard segment can be a driving

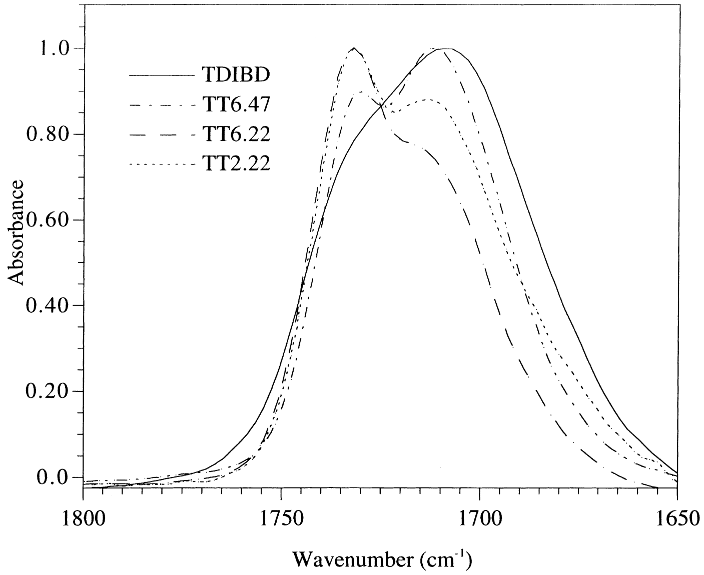


Fig. 1. FTir C=0 stretching region of TDI based polyurethanes.

factor in the phase separation of polyurethane elastomers. The less phase separated structure obtained in MDI based polymers could be explained with a viscosity mobility argument as explained by Li et al. [14].

Chu et al. [15] have studied the microphase separation kinetics in aromatic isocyanate based poly (ether-urethanes) by small angle X-ray scattering (SAXS). They conclude that phase separation kinetics are much faster in polyurethanes with larger soft segments. Similar conclusions, using dynamic mechanical thermal analysis (DMTA) [16] and DSC [17–20], had also been previously reported.

In conclusion, T_{gs} is found to exhibit a strong dependence on urethane concentration. This is suggested as due to extensive hard segment mixing with the soft segment phase. The decrease in T_{gs} with increasing soft segment molecular weight indicates a higher phase separation in systems having longer soft segments. The decrease in T_{gs} in TDI based polyurethanes compared with those based on MDI, suggests a better phase separation in TDI based poly (ether-urethanes).

3.2. FTir studies

FTir spectra in the carbonyl stretching vibration region (1800–1650 cm^{-1}) for the synthesised polyurethanes are shown in Figs. 1 and 2. All the spectra present two major spectral components [3]. Thus, the band at higher frequencies (1731 cm^{-1}) can be assigned to 'free' carbonyl groups

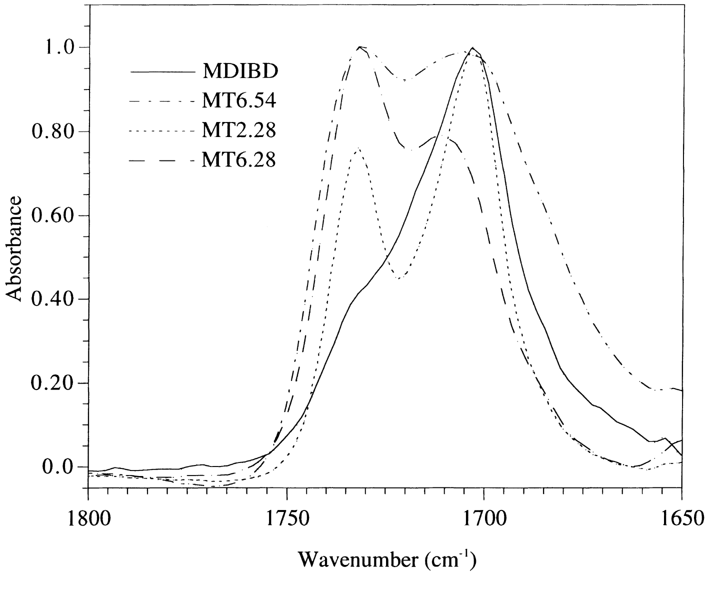


Fig. 2. FTir C=0 stretching region of MDI based polyurethanes.

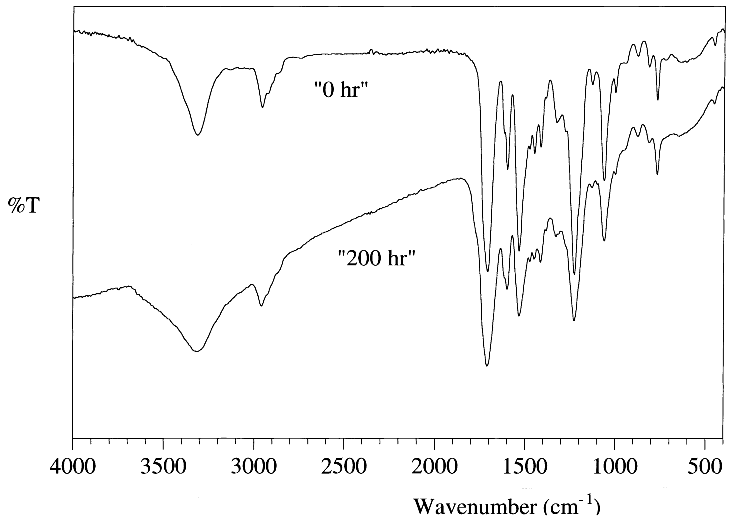


Fig. 3. FTir spectra of TDIBD before and after irradiation.

and the other one at lower frequencies (1712 cm^{-1}) is due to hydrogen bonded carbonyl groups.

If we compare the spectra displayed in Fig. 1, it can be seen that non-segmented TDIBD presents the largest contribution of the hydrogen bonded carbonyl band. As hydrogen bonding association in the hard segment takes place between carbonyl and N–H groups, in TDIBD almost all the carbonyl groups are associated by hydrogen bonding with the N–H groups. In the segmented polymers, however, the ether oxygen of the polyether block competes with the urethane carbonyl group for hydrogen bonding with the urethane N–H group [21]. In the segmented polymers, every time that an ether group of the soft segment forms a hydrogen bond with the N–H group, a carbonyl group of the hard segment is freed.

This competition between the ether oxygen and the carbonyl group to form hydrogen bonds with the N–H is reflected in the carbonyl stretching region of poly(ether-urethanes). As the hard/soft segment interaction increases, the bonded carbonyl band decreases. In other words, the more phase separated structures will have a larger contribution of the hydrogen bonded carbonyl groups.

In order to determine the effect of the molecular weight of the soft segment on the urethane association, we need to compare two polymer samples synthesised with the same percentage of rigid segment but from different molecular weight soft segments.

As can be seen in Fig. 1 where the spectra of TT6.22 and TT2.22 are compared, TT6.22 has a larger contribution of the ‘free’ carbonyl band than TT2.22. Therefore, in TT6.22 there is more phase mixing between the soft and the hard segments. This effect, due to the attachment of the soft

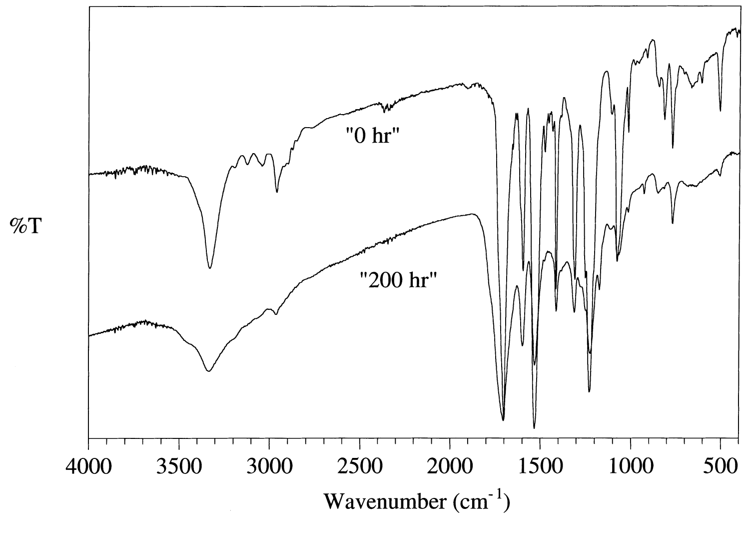


Fig. 4. FTir spectra of MDIBD before and after irradiation.

Table 3
Infrared characteristic frequencies of poly(ether-urethanes)

Frequency (cm^{-1})	Relative intensity[a]	Main assignments[b]
3420	vw,sh	υ (N–H) free
3320	vs	υ (N–H) associated
3050	w	Overtone of amide II band
2800	m	υ C–H in polytetramethylene oxide
1730	s	υ C=0 free
1707	vs	υ C=0 associated
1600	m	υ C=C in aromatic ring
1533	s	υ C–N + δ N–H (amide II)
1475	w	δ CH_2
1263	s	δ N–H + υ C–N (amide III)
1110	s	υ 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	Aromatic in plane deformation vibration in *p*-rings
513	vw	Aromatic o.o.p. deformation vibration in *p*-rings
455	vw	Aromatic o.o.p. deformation vibration in 1,2,4 rings

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] υ: Stretching vibration, δ: in plane deformation vibration, δ oop: out of plane deformation vibration, ω: wagging deformation vibration.

segments to stiffer urethane groups, has already been demonstrated by DSC [22]. The same comparison can be done with MDI based polyurethanes, MT6.28 and MT2.28 (Fig. 2).

The effect of the variation in hard segment concentration without modifying the soft segment molecular weight can also be seen in Figs. 1 and 2. The contribution of the associated carbonyl band decreases as the hard segment content decreases.

3.3. Photodegradation results

3.3.1. MDI and TDI based non-segmented polyurethanes

The infrared spectra of the two non-segmented polyurethanes (MDIBD and TDIBD) before and after irradiation are shown in Figs. 3 and 4.

Table 3 describes the infrared characteristic frequencies of aromatic polyurethanes [22].

The predominant effect of UV exposure on both systems is a decrease in the urethane characteristic absorption bands (1720 and 1533 cm^{-1}) together with a broadening of the band at 3200 cm^{-1}. This broadening can be attributed to the formation of hydroxylated photoproducts.

These experimental results support the photodegradation mechanism proposed by Gardette and Lemaire [6]. The rupture of the urethane linkage in the exposed samples suggests that a Photo-Fries type reaction has taken place in both samples. As a consequence of this reaction, changes in the substitution pattern of the aromatic ring are observed in the FTir spectra. If we study the 900–400 cm^{-1} infrared region, MDI based polyurethanes show a decrease of the bands centred at: 818 cm^{-1} (aromatic =C–H out-of-plane deformation vibration in *p*-disubstituted ring), 612 cm^{-1} (in-plane aromatic ring deformation vibration in *p*-disubstituted ring) and 513 cm^{-1} (out-of-plane aromatic ring deformation vibration in *p*-disubstituted ring), together with the appearance of two new bands at 840 cm^{-1} (aromatic =C–H out-of-plane deformation vibration in 1,2,4 trisubstituted ring) and 455 cm^{-1} (aromatic ring out-of-plane deformation vibration in 1,2,4 trisubstituted ring). In the case of TDI based polyurethanes, the presence of 20% of 2,6 TDI isomer, makes the aromatic =C–H out-of-plane region very complex and difficult to make precise assignments. However, in the aromatic ring deformation vibration region, a decrease of the band intensity at 456 cm^{-1}, due to 1,2,4 ring trisubstitution, can be clearly observed.

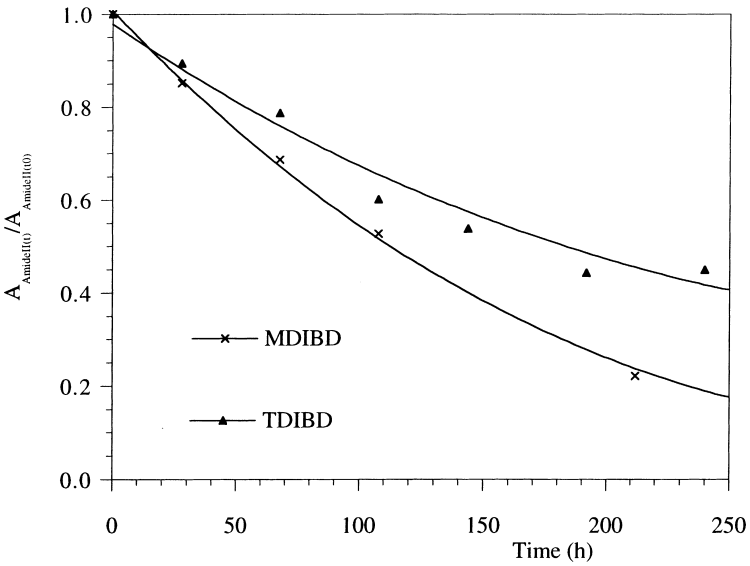


Fig. 5. Normalised decrease of the amide II band for TDIBD and MDIBD polyurethanes as a function of the irradiation time.

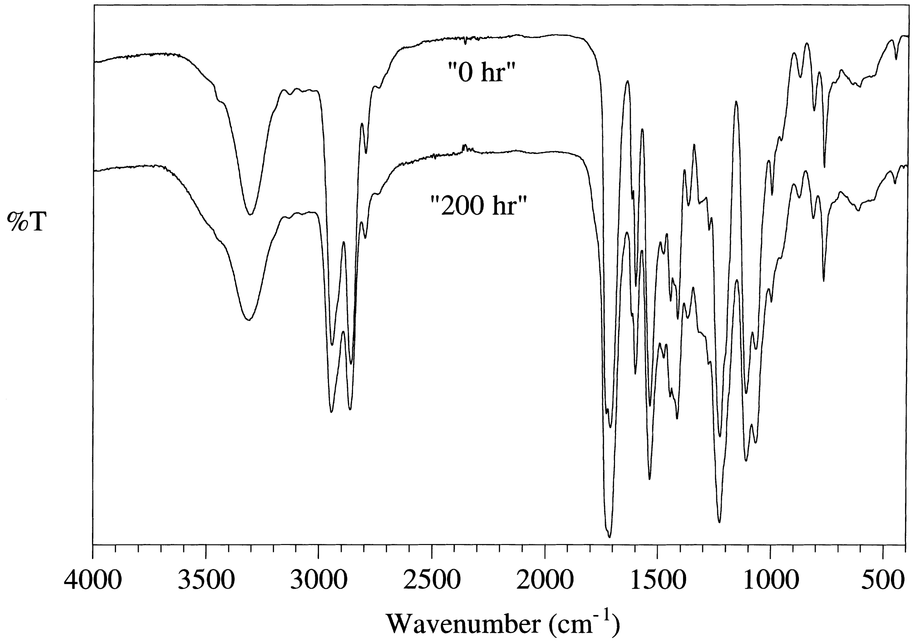


Fig. 6. FTir spectra of TT6.47 before and after irradiation.

These infrared changes observed in MDI and TDI based polyurethanes are indicative of the Photo-Fries reaction.

In order to follow the evolution of the photodegradation by means of FTir measurements, we have calculated the area of the amide II band, which is directly related to the urethane linkage, at different exposition times. We have normalised the results to the value of the corresponding band area of the non-exposed sample.

If we compare the decrease of the amide II band for MDIBD and TDIBD samples (Fig. 5), we notice that the decrease is higher in MDIBD. The decrease of the amide II band in MDI based polyurethanes accounts for two different processes: C–N bond photolysis and oxidation of the central methylene carbon atom. The oxidation of this methylene group can lead to the formation of quinone-diimide structures as well as benzoic acid end groups. Taking into account these considerations, as in TDIBD the induced oxidation process can not take place, the observed decrease of the amide II band reflects only the urethane linkage

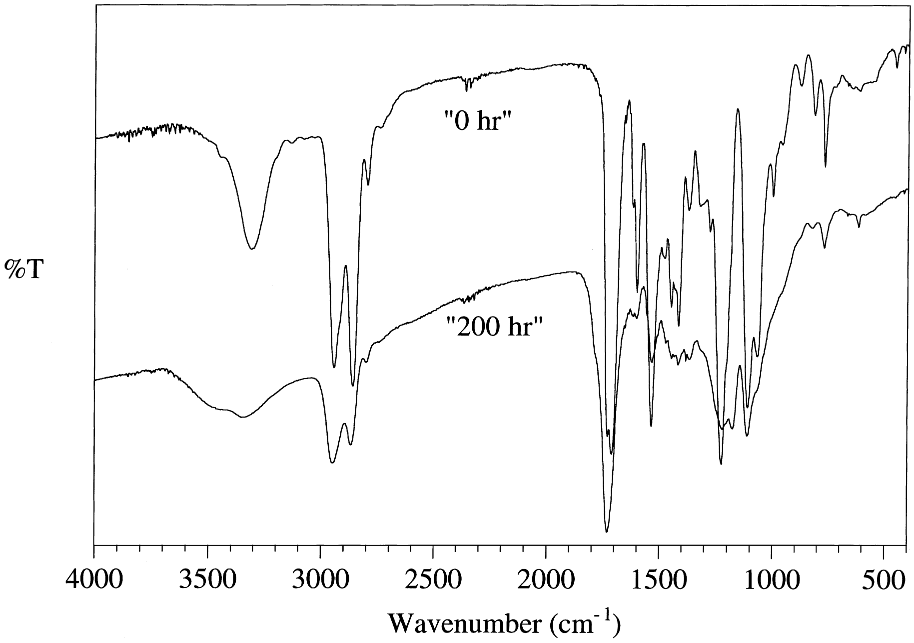


Fig. 7. FTir spectra of TT2.22 before and after irradiation.

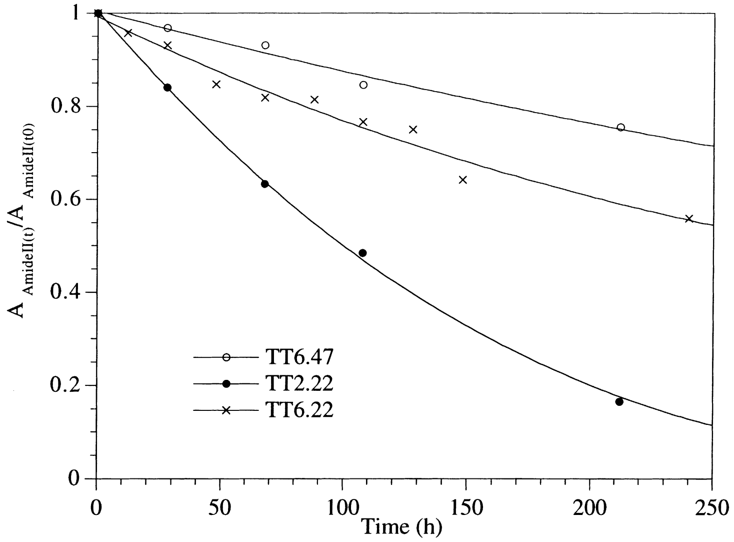


Fig. 8. Normalised decrease of the amide II band for TDI based segmented polyurethanes as a function of the irradiation time.

photolysis. This is the reason why the decrease is higher in MDIBD than in TDIBD.

3.3.2. TDI based segmented polyurethanes

FTir spectra of TT6.47 and TT2.22 samples and their evolution with the irradiation time are shown in Figs. 6 and 7. The modifications of the infrared spectra can be separated into those concerning the polyether component and those of the urethane functions.

In the ether segments, a reduction in the intensity of the band at 1110 cm^{-1} (υ C–O–C in ether linkage) can be observed, which strongly suggests the rupture of the ether linkage as a result of the exposure to UV radiation. This behaviour is consistent with the general photo-oxidation scheme for polyethers [8].

In these spectra we can also observe a substantial loss of urethane structures indicated by the decrease in the intensity of the bands at 3320 and 1532 cm^{-1}. An evolution of the bands in the 900–400 cm^{-1} region similar to that of non segmented TDIBD is also observed.

The results of the amide II band evolution as a function of the irradiation time are shown in Fig. 8. As can be seen, the highest decrease rate of the amide II band is displayed by the sample with the highest soft segment molecular weight (TT2.22). In the case of the two segmented polyurethanes based on PTMO650, the reduction of the

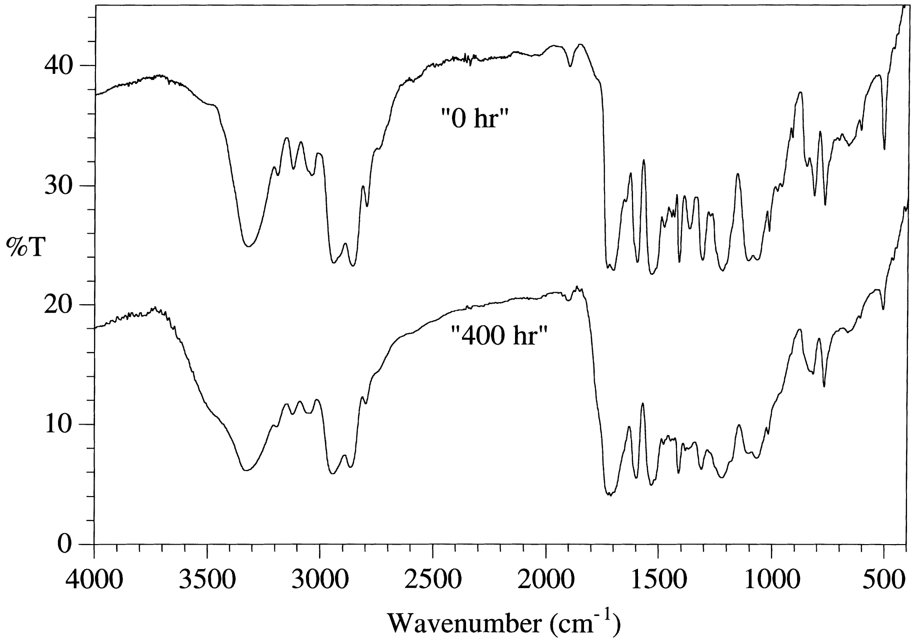


Fig. 9. FTir spectra of MT6.54 before and after irradiation.

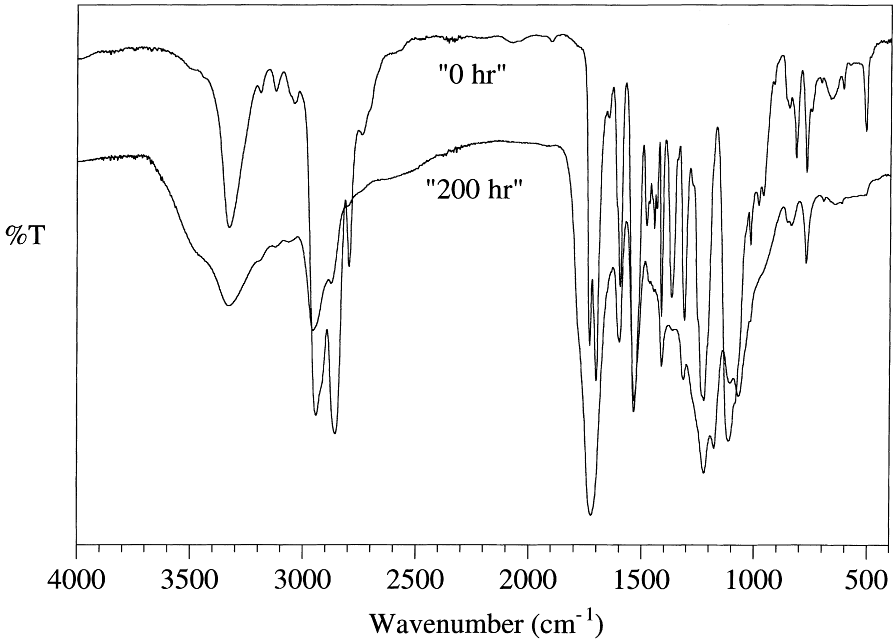


Fig. 10. FTir spectra of MT2.28 before and after irradiation.

amide II band increases as the percentage of soft segment increases.

If we compare the decrease of the amide II band for samples having the same hard segment content but different soft segment molecular weight (TT6.22/TT2.22), we see that the higher molecular weight based sample shows a higher decrease in the amide II band. As these two samples have the same hard segment percentage, the observed differences indicate that the soft segment molecular weight plays a major role in the photodegradation of urethane structures.

DSC and FTir results indicate that in sample TT2.22, the interaction between the hard and the soft segments is lower than in TT6.22. Therefore, it seems that the higher photodegradation resistance showed by sample TT6.22 is related with the higher degree of phase mixing. There is a stabilising effect between the urethane hard segments and the ether soft segments which increases when increasing the hard/soft segment interaction. This statement has already been proposed by several authors from thermal degradation studies for this type of system [23].

3.3.3. MDI based segmented polyurethanes

FTir spectra of MT6.54 and MT2.28 samples and their evolution with the irradiation time are shown in Figs. 9 and 10.

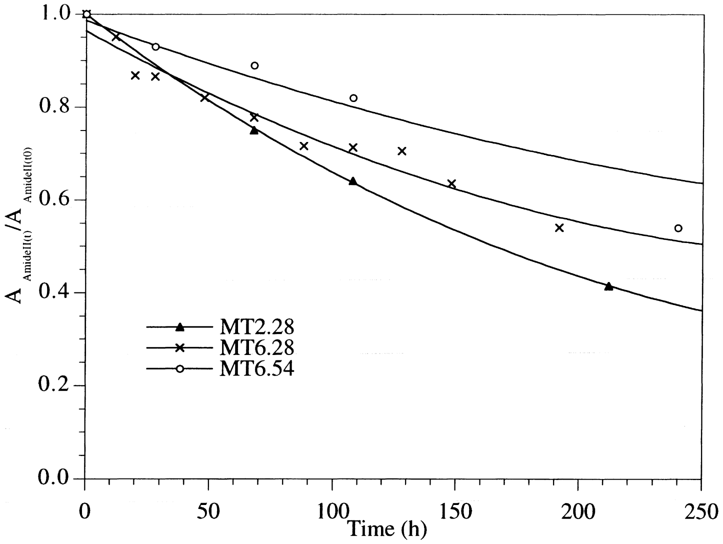


Fig. 11. Normalised decrease of the amide II band for MDI-based segmented polyurethanes as a function of the irradiation time.

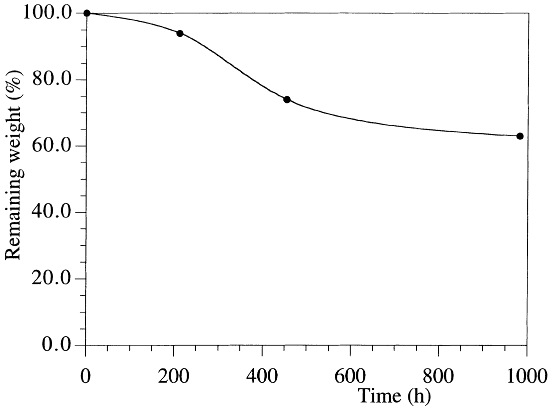


Fig. 12. Weight loss for TT2.22 as a function of the irradiation time.

As in TDI based segmented polyurethanes, a decrease of the intensity of the band at 1110 cm^{-1} (υ C–O–C in ether linkage) can be seen. In these spectra, we also observe a substantial loss of urethane structures indicated by the decrease in the intensity of the bands at 3320 cm^{-1} and 1532 cm^{-1}. In addition, the evolution of the bands in the 900–400 cm^{-1} region is similar to that of non-segmented MDIBD.

Fig. 11 depicts the decrease of the amide II absorption band for MDI based polyurethanes. Here again, the higher the soft segment concentration the higher the rupture of the C–N linkage. The role of the soft segment molecular weight can be visualised by a higher decrease of this band shown by MT2.28.

The effect of the soft segment percentage and molecular weight on the photodegradation behaviour of MDI based segmented polyurethanes is the same as the obtained for TDI based segmented polyurethanes. Therefore, the argument used for describing those samples can be used here.

3.3.4. Weight loss measurements

The results of sample weight loss as a function of the irradiation time are shown in Figs. 12 and 13.

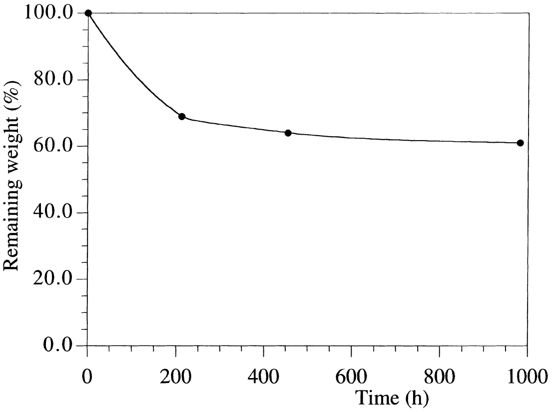
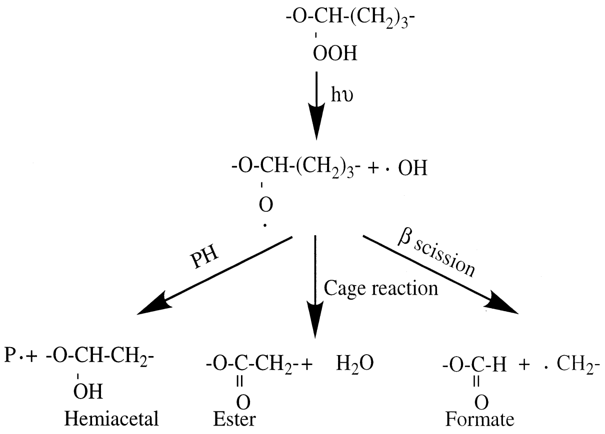


Fig. 13. Weight loss for MT2.28 as a function of the irradiation time.



Scheme 1.

The weight loss experienced only by the high molecular weight soft segment based polyurethanes must be related to the photo-oxidation of the ether soft segments.

Scheme 1 shows the photo-oxidation mechanism for PTMO, proposed by Lemaire [8]. According to these authors, the evolution of the alkoxy radicals is responsible for the formation of formate groups. These groups are re-oxidised in a second phase leading to low molecular weight photoproducts [7] which can migrate out of the polymer.

The stability toward weight loss shown by low molecular weight soft segment polyurethanes can be due to the accumulation of high photostationary concentration of hydroxy groups or/and the stabilisation of these groups, favoured by a higher phase mixing of these systems.

4. Conclusions

The introduction of soft segments in formulations based on TDI or MDI, makes these systems behave differently as a function of soft segment molecular weight. Thus, for PTMO650 based polyurethanes the susceptibility toward photodegradation is reduced due to a stabilisation effect as a consequence of a high interphase mixing. For these systems the photodegradation extent increases as soft segment content increases. The different behaviour observed in TT6.22/TT2.22 and MT6.28/MT2.28 can be explained upon the basis of a higher effect of molecular weight than soft segment content. Therefore, in segmented polyurethanes the extent of the urethane group rupture increases as both soft segment molecular weight and soft segment percentage increase.

Phase mixing and hence urethane group photodegradation are more affected by soft segment molecular weight than by soft segment percentage. Samples having higher soft segment molecular weight are more phase separated and, therefore, the extent of the rupture of the urethane linkage is higher than in low molecular weight soft segment based polyurethanes.

Acknowledgements

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