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Thermal oxidation of the methylene diphenylene unit in MDI-TPU

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Abstract

Improving the heat resistance of thermoplastic polyurethane (TPU) is still a challenging task. Therefore, a better understanding of the processes contributing to thermal aging of these materials is of crucial importance. Previous investigations showed that thermal oxidation of the soft segments plays a major role in chemical aging of TPU. With the help of several analytical methods, we could prove that there is also a contribution by thermal oxidation of the methylene diphenylene (MDI) units, producing benzophenone derivatives. The amount of rigid material diminishes as a consequence of the MDI oxidation. The size as well as the amount of the rigid phase was found to be only one third after annealing in air at 150°C. We conclude that besides oxidation of the soft segments, oxidation of the MDI units plays a major role in chemical aging of TPU. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Segmented polyurethanes; TPU; MDI

1. Introduction

To improve the heat resistance of TPU, a better understanding of the processes contributing to thermal aging of these materials is necessary. Previous investigations showed that the material suffers from thermal oxidation. From the literature [1–9] it is known, that oxidation of the soft segments plays a major role in aging of polyether based polyurethanes. This finally leads to chain cleavages, i.e. decrease of molecular weight. As a result, the mechanical properties like tensile strength and elongation decrease with time. The oxidation of polyethers, e.g. polytetrahydrofuran (PTHF), usually starts at the α-position of the ether bridge and proceeds via a hydroperoxide. This finally leads to chain scission, thereby reducing the molecular weight and consequently worsening the mechanical properties. Aldehydes and formates can be identified as products resulting from oxidation. In contrast to polyethers, polyesters or polycarbonates are by far less sensitive to oxidation.

Thermoplastic polyurethanes are block copolymers and owe their elasticity to their biphasic morphology. The elastomer consists of phase separated rigid and soft blocks, called rigid and soft phase. The soft phase, composed of polyether or polyester polyols, gives the material its flexibility, whereas the rigid phase provides the elastic recovery by acting as a physical crosslink. Here the question arises, whether the aging of TPU can be attributed to the oxidation of the soft phase alone or whether the rigid phase is also affected. In literature some authors report about the photo-oxidation of rigid segments [10–12]. The products obtained from this reaction are supposed to have quinone structures. It was stated that photo-oxidation occurs at the methylene bridge of the MDI unit by forming a hydroperoxide. The hydroperoxide was proposed to convert to a quinone structure (Fig. 1) [10–12].

In contrast to these investigations, we were interested in pure thermal, i.e. non-photochemical oxidation. Therefore, we investigated the oxidation processes occurring under thermal exposition only, without any irradiation. Since our goal was to focus on the fate of the rigid phase components upon thermal aging, we chose TPU based on polyester instead of polyether soft blocks in order to minimise thermal aging of the soft phase. The oxidation products of the rigid phase were identified by analysing the aged TPUs with spectroscopic methods (NMR and IR) and additionally by examining the hydrolysis products of the aged TPUs as described below in detail.

2. Analysis of aged MDI-TPU

In order to investigate the oxidation of the methylene bridge in MDI based TPU, a polyester based MDI-TPU was kept at 150°C in air for 77 days and the corresponding oxidation products were identified and quantified by various

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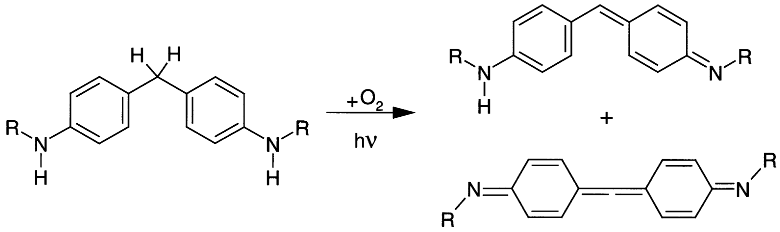


Fig. 1. Formation of quinone-type structures upon photooxidation.

analytical methods. The results of these methods, solid state NMR, IR and hydrolysis with subsequent GC–MS analysis, are presented here.

2.1. Solid state NMR

Solid state NMR is used to investigate both, changes in chemical and physical structure during thermal aging of TPU.

High-resolution solid state NMR (CP/MAS NMR) yields carbon-13 spectra with distinct signals for the various chemical positions in a molecule and is similar to solution NMR in this respect [13]. CP/MAS NMR can thus be used as an analytical tool to reveal chemical structures. This chemical type of information has been combined with solid state ^{1}H-NMR relaxation measurements, T_2(H), on stationary samples in order to differentiate with respect to molecular dynamics. T_2(H) relaxation measurements are used to determine the amount of mobile and immobile material in the dynamically heterogeneous TPU. ^{1}H line width can directly be correlated with the ^{13}C spectrum in a two-dimensional (2D) solid state NMR measurement ("WISE"—wide line separation experiment [14,15]). This experiment links chemical structure and molecular mobility and is used to investigate the effect of chemical aging on the phase structure.

Furthermore, several experiments are run which allow to allocate chemical structures to domains applying a spatial criterion: $T_{1\text{rho}}$(H) of the hydrogen nuclei as detected via ^{13}C CP/MAS [16,17] reveals where a certain chemical structure is located, whether it belongs to the rigid or to the soft phase. In addition, we get information about the size of the phase from spin diffusion after dipolar filtering [15,18]. In both cases, it is spin diffusion and thus a spatial criterion which applies.

2.1.1. Chemical structure (CP/MAS NMR)

High-resolution ^{13}C CP/MAS solid state NMR spectra were acquired at 7 T (Bruker MSL300) at a spinning rate

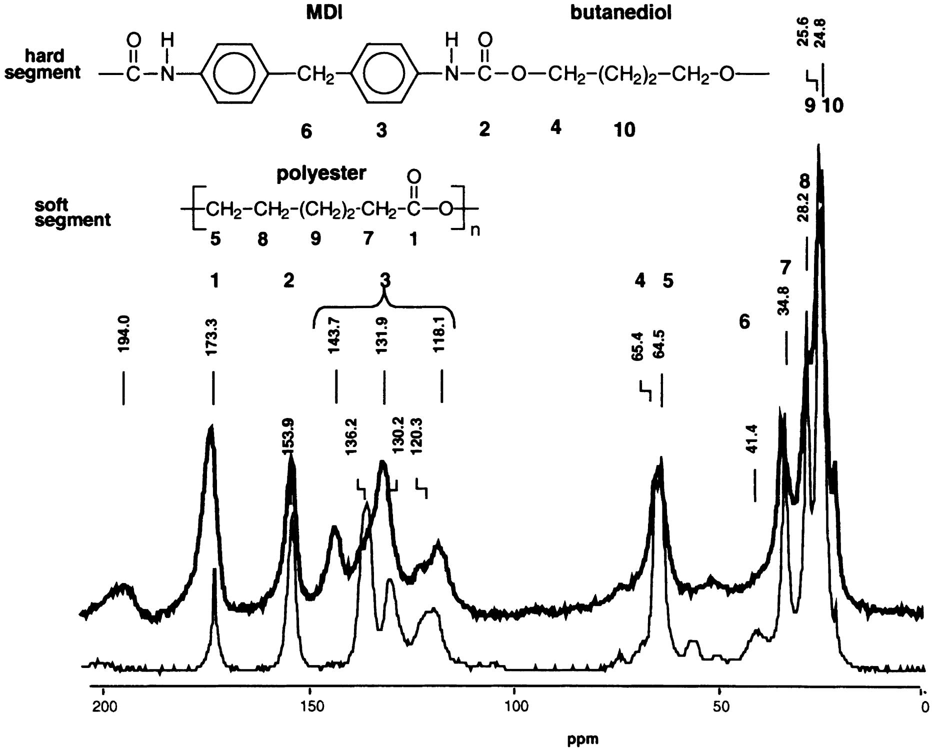


Fig. 2. ^{13}C CP/MAS spectra of the pristine (lower trace, thin line) and the aged (upper trace, bold line) MDI-TPU.

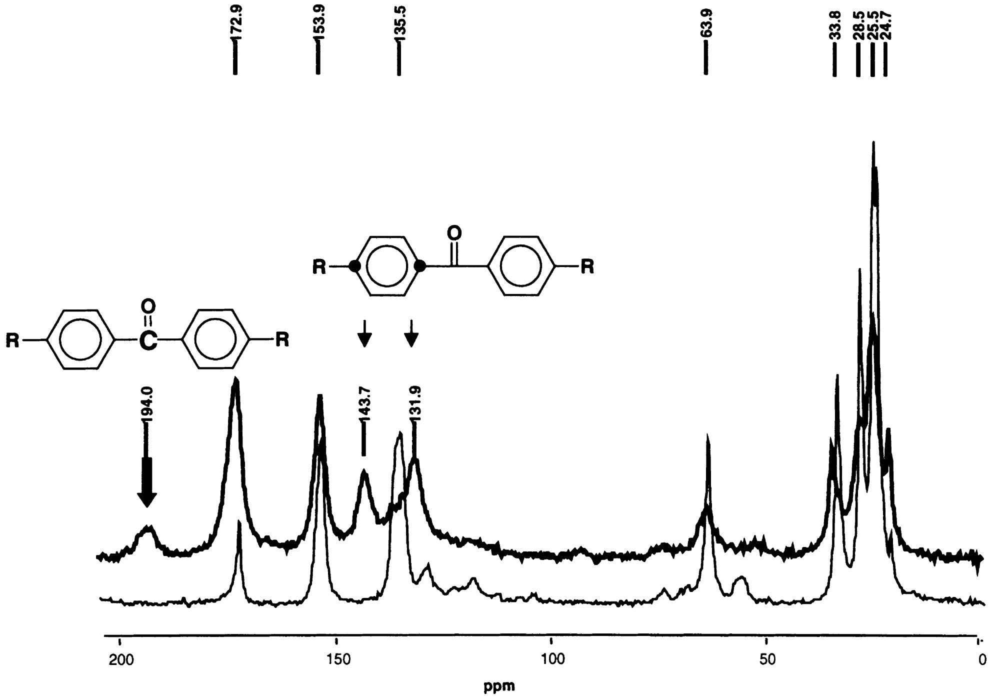


Fig. 3. ^{13}C CP/MAS with non-quaternary suppression: pristine (lower trace, thin line) and aged (upper trace, bold line) TPU.

of 6 kHz, with cross-polarisation (CP) and dipolar decoupling during acquisition (B_1 50–60 kHz). Spinning side bands from MAS are marked "SSB". A rather long CP contact of 3 ms is used to ensure sufficient signal intensity from those carbons belonging to the flexible component. The spectra thus generated represent the structures in a quantitative style as long as we restrict ourselves to the rigid part of the sample. A delayed decoupling (40 ms) suppresses signals with strong dipolar coupling, i.e. all carbons located in the rigid phase with a directly attached hydrogen. This non-quaternary suppression (NQS) experiment is used to assign non-quaternary carbons in the spectrum. "Counting" them gives an idea of whether changes, that are observed in the aromatic region, originate from a variation in the substitution pattern of the aromatic MDI-rings. Storing ^{13}C magnetisation after CP for 2 s parallel/anti-parallel to the B_0 field before detection selects immobile C–H segments. Signals from highly mobile soft segment are suppressed and spectral density in the frequency range (MHz) for suppressed signals is indicated.

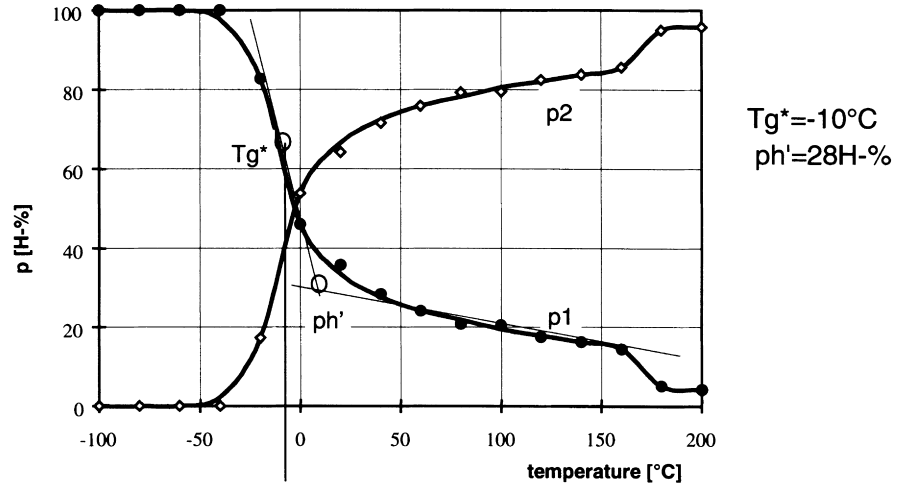
The CP/MAS spectrum of a MDI based TPU allows to identify the various chemical structures (Fig. 2). Thermal treatment in air for 77 days at 150°C changed the spectrum in several aspects. A new signal appears at 194.0 ppm. Furthermore, the pattern in the aromatic region changes drastically.

The NQS experiment indicates a shift of part of the quaternary carbon from 135.6 to 143.1 ppm (Fig. 3). However, the intensity ratio of the signal at around 154 (urethane groups) to that of the quaternary aromatic carbons did not change upon thermal aging. All signals became much broader and spectral resolution are partly lost.

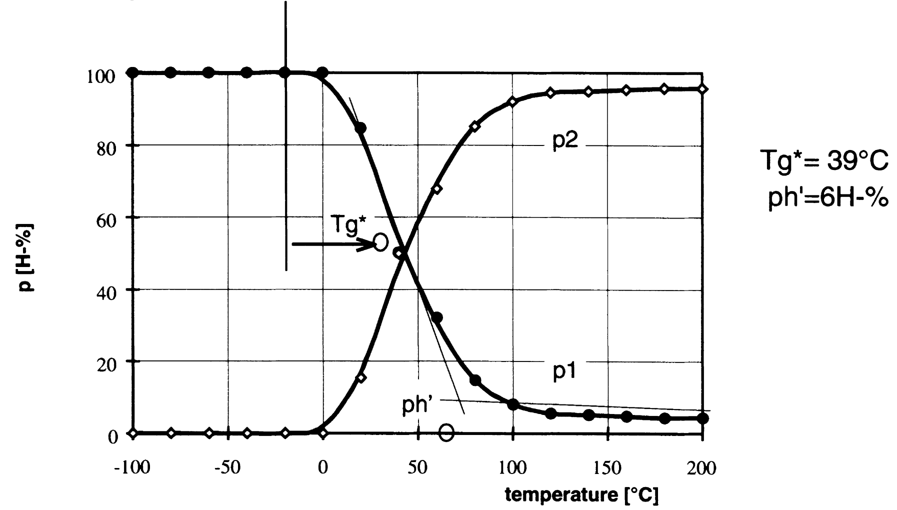
The changes can be explained by an oxidation of the central methylene unit in the MDI to a keto unit. This interpretation is supported by several facts and has been confirmed by other techniques. First of all, 190 ppm is the typical location of a ketone next to sp^2 carbons. A $>C{=}O$ on an aliphatic chain (in the soft segment) will appear further down-field, i.e. at around 209 ppm, and can be excluded. The postulated central keto group in the MDI unit provides a straightforward explanation for the change in chemical shift observed in the aromatic region of the aged, MDI based TPU. The keto group typically shifts the neighbouring quaternary carbon C(1,1′-) upfield by 4–5 ppm and the 4,4′-position downfield by the same amount. This should result in two signals for the quaternary carbons separated by about 10 ppm. In fact, signals at 143.1 ppm (4,4′-) and at 131.2 ppm (1,1′-) are found (Fig. 3).

Whereas the position of the signals changed, the intensity of these aromatic quaternary carbons remains nearly unchanged (using the urethane signal as an internal reference). This excludes a changed pattern of substitution at the aromatic ring as an alternative explanation for the changes in chemical shift. The intensity of the evolved keto signal was about 1/4 of that of the urethane group, thus about half of the methylene groups of MDI must have been converted to keto groups upon aging the material in air for 77 days at 150°C.

Compared to the pristine material the signals in the ^{13}C spectrum of the aged sample are broadened. This broadening can either be a consequence of molecular dynamics



a) MDI-TPU, pristine



b) MDI-TPU, aged (77d 150°C)

Fig. 4. ^{1}H transverse relaxation T_2(H) of the pristine (top) and aged (bottom) TPU.

(homogeneous broadening), or it can be due to changes in the chemical structure causing slight variations in chemical shift (inhomogeneous broadening). The latter explanation applies to the aromatic region of the spectrum as the methylene units in part of the MDI units are oxidised. However, the line width of the signals from the soft segment is predominantly influenced by molecular mobility. The glass transition temperature of the soft phase rises with increasing oxidation of the MDI units (see also in Section 2.1.2). Line widths of the soft segments of the two samples have to be compared at temperatures equidistant to their respective glass transitions, not at equal absolute temperatures. Comparing the spectrum of the pristine sample, measured at 298 K, and the aged sample, recorded at 343 K, we notice that the line widths of the soft segments are indeed identical. We take this as an indication that the chemical structure of the polyester soft segments is largely preserved during oxidation of this MDI based TPU, but their mobility in the soft phase is reduced.

2.1.2. Molecular mobility and rigid phase content (^{1}H relaxation, WISE)

A ^{1}H relaxation measurement of both MDI samples, before and after aging, is shown in Fig. 4. The sample is frozen in at low temperatures. A mobile component p_2 (long T_2) only appears as the temperature exceeds the glass transition of the flexible component[1]. We observe an increase of the NMR glass transition temperature upon aging. The glass transition is shifted from about -10°C initially to about $+39$°C after 77 days (Fig. 4).

The content of immobile material, $p_1 = 1 - p_2$,

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[1] The temperature of glass transition is about 30 K higher in NMR than in DSC due to the higher frequency of measurement.

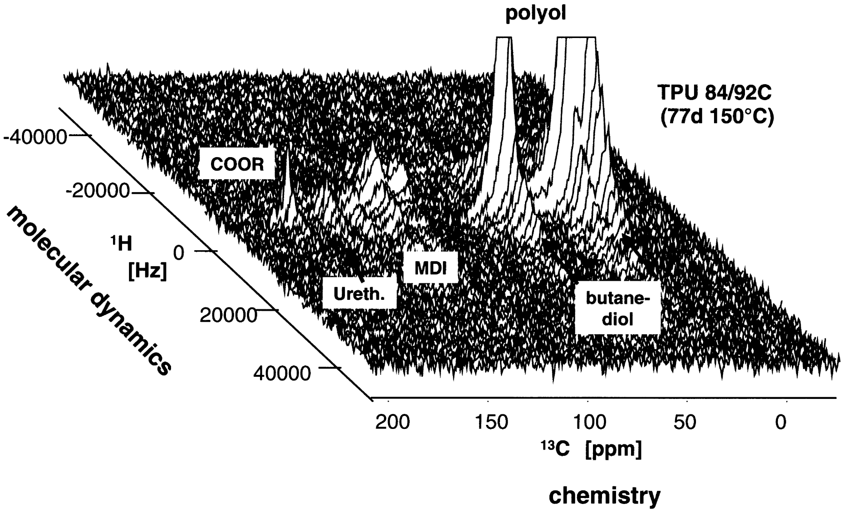

Fig. 5. Two-dimensional WISE spectrum of the aged MDI-TPU.

decreases rather continuously above the glass transition. This behaviour is typical for urethane based materials in contrast to urea containing PU-materials. p_1 gradually reaches a final value of 15% (^{1}H) in the pristine sample as the temperature is raised; p_1 of the aged sample drops down to 5%. This indicates, that the rigid phase content is drastically reduced by thermal aging. It may be argued, that the dependence of p_1 on temperature is influenced by thermal history. There is a drop in p_1 of the pristine sample around 160°C as a consequence of its storage at 150°C for 20 h, for example. For a comparison of the rigid phase content p_1 before and after thermal treatment, we wish to eliminate the influence of thermal history. This is accomplished by not comparing $p_1(T)$ directly, but the extrapolated rigid phase content p_h' instead. p_h' is obtained from the intercept of the tangent to the glass transition with a straight line following p_1 above T_g (see p_h' in Fig. 4). In fact, p_h' drops from 28 to 6% in a MDI-TPU due to thermal treatment.

It should finally be mentioned that the mobility of the rigid phase (T_{21}) increases upon aging: T_{21} is 15 ms in the untreated sample but 22 ms in the aged sample. A T_{21} greater than 20 ms is more than what is usually found for a really rigid phase. Thus T_{21} indicates the presence of some mobility in the “rigid” phase.

The WISE experiment [14,15] is a 2D NMR experiment, run under MAS conditions. WISE directly correlates a ^{13}C high-resolution spectrum (Section 2.1.1) with T_2(H) relaxation of the surrounding ^{1}H nuclei and thus links the information on chemical structure to molecular mobility. A short T_2(H) of a rigid structure results in a ^{13}C signal which is broad along the ^{1}H axis in the WISE experiment. We detect an immobile component (broad line along ^{1}H axis) in the 2D correlation experiment at the location of the aromatic signals (120–145 ppm) as well as at the positions of the urethane (154 ppm) and butanediol (65 and 26 ppm) in the aged sample (Fig. 5).

The WISE experiment involves CP, during which spin diffusion will take place. Spin diffusion is very fast in the aged sample due to the minute size of the rigid phase (see Section 2.1.3). In order to avoid the effects of spin diffusion a short contact time (0.5 ms) has to be used to reveal the rigid phase. As the amount of rigid phase is small in this sample, and with a short contact time used, the signal to noise ratio is rather low for the rigid segment: We do not see a change in line shape as we step through the WISE spectrum parallel to the carbon-13 axis and there is no change in the contribution of the signal at 143.1 ppm (4,4′-position of the oxidised MDI) visible either. Therefore, it cannot be decided from the WISE data, whether the oxidised MDI units belong to the rigid or to the soft phase. The WISE experiment however confirms, that there is some residual amount of rigid phase in the aged sample. We suggest that the benzophenone units produced by thermal aging (see Section 2.1.1) impair the segregation of rigid and soft phase. Glass transition temperature of the soft phase is heavily raised presumably due to partial mixing of soft and “oxidised rigid” segments. The limiting amount p_1 of segregated rigid segments forming the rigid phase at high temperature is lowered from 15 to 5% only. The existence of immobilised structures is confirmed by a 2D correlation experiment (WISE), showing that aromatic rings, butanediol and urethane groups constitute the rigid phase after thermal treatment. However, segregation is not as neat as it was in the pristine sample.

2.1.3. Spatial information from NMR (T_{1rho}(H), spin diffusion)

Proton relaxation measurements (Section 2.1.2) indicate a change in T_g and in phase structure due to thermal aging. Therefore, the question arises if a segregated rigid “phase” remains at all after oxidation. Experiments indicate that this is true indeed. First of all, the sample evidently still contains an “immobile” component p_1, although only about 1/3 of the initial amount remains (see Section 2.1.2). Secondly, a

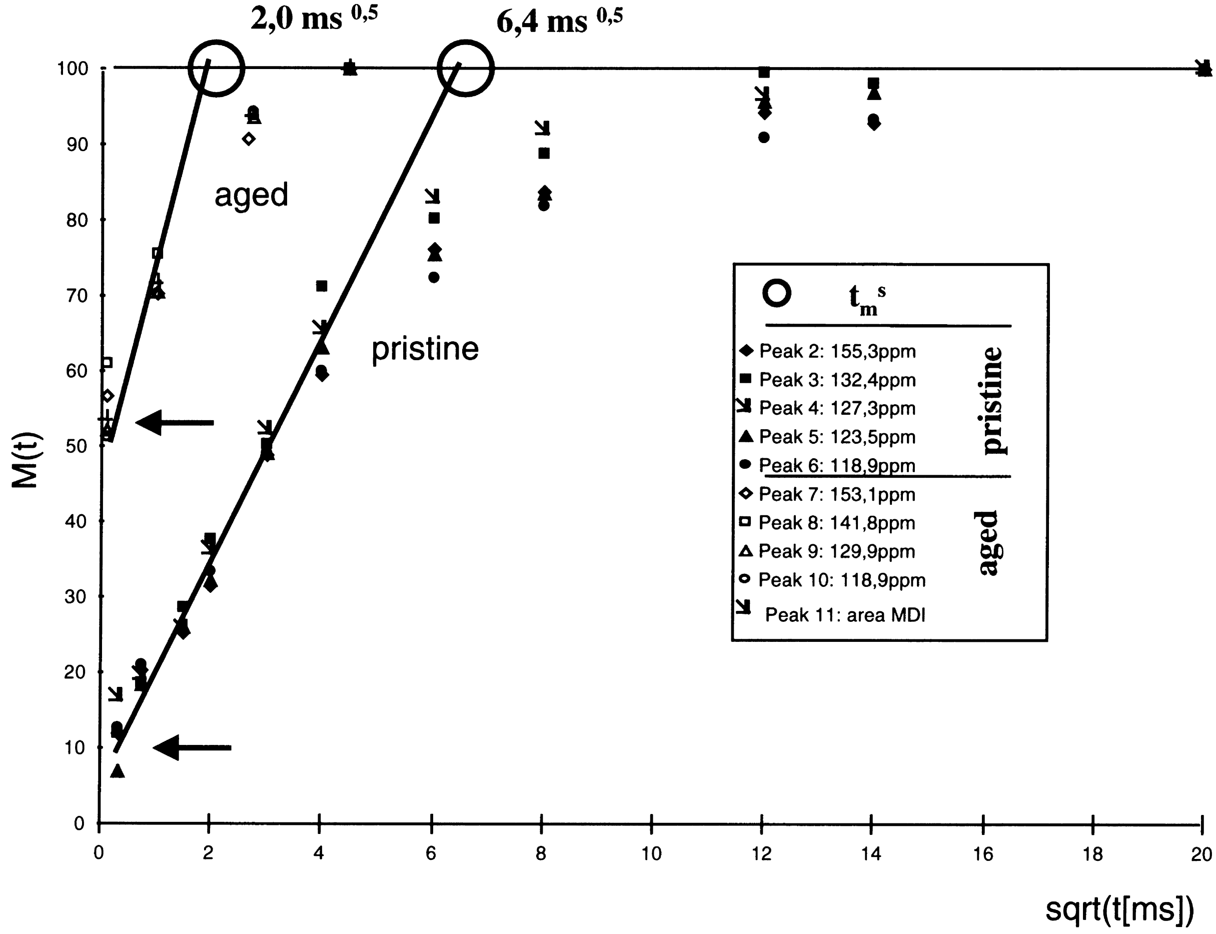

Fig. 6. Spin diffusion of magnetisation into the rigid phase (^{13}C CP/MAS, 323 K).

$T_{1\mathrm{rho}}$(H) detected via ^{13}C may be used to prove that the immobile component forms a separate phase. As $T_{1\mathrm{rho}}$(H) is averaged over a distance of approximately 1 nm by spin diffusion, i.e. an exchange of spin energy among the ^{1}H spins during spin-locking, a distinct $T_{1\mathrm{rho}}$(H) of a separate "phase" will only be found, if this phase has a diameter of at least 1 nm. At 343 K, a $T_{1\mathrm{rho}}$(H) of (2.3 + 0.3) ms for the signals of the soft segments and another $T_{1\mathrm{rho}}$(H) of (1.1 + 0.2) ms for the rigid segments can clearly be distinguished in the aged MDI-TPU. Therefore, a residual amount of rigid segments must be present, forming aggregates. Unfortunately, the difference in $T_{1\mathrm{rho}}$(H) is too small to decide whether only a central core of non-oxidised rigid phase is preserved as "rigid phase", or whether the oxidised material remains part of the rigid phase as well. The $T_{1\mathrm{rho}}$(H) behaviour of the signal at 143.1 ppm did not allow a clear assignment of the newly formed ketone to the rigid or soft phase for sensitivity reasons as well.

The dimension of the rigid phase can be estimated from a spin diffusion experiment after dipolar filtering [15,18] (1 filter cycle, spacing 12 μs, 323 K). Only about 50% of the aromatic carbons are filtered out in the aged sample (Fig. 6, see ← at mixing time zero), whereas nearly the whole MDI signal (approximately 90%) can be suppressed by this filter setting in the pristine sample. This confirms dynamic heterogeneity in the aged sample. Part of the MDI behaves "mobile", and this amount is about the same as the amount of the oxidised MDI. Another striking observation is how polarisation spreads in the pristine and oxidised samples: a characteristic mixing time t_m^s is obtained from the intercept of the initial slope of magnetisation with the 100% level [18]. A t_m^s of only 4 ms in the oxidised sample has to be compared to t_m^s around 40 ms before heat treatment. The short t_m^s in the oxidised sample indeed indicates that the domains are very small. The size of the rigid phase, d_A, may be estimated from the initial slope using the relation $d_A = \epsilon/f_B(4Dt_m^s/\pi)^{0.5}$. If we assume a reasonable model (dimension $\epsilon = 2$ for a lamellar structure, average diffusion coefficient $D = 0.4$ (nm^2/ms)), d_A can be calculated as d_A (nm) $= 1.4/f_B$ (t_m^s (ms))$^{0.5}$. The amount of soft phase, f_B, was determined by a spin diffusion experiment with direct detection of the soft phase by ^{1}H acquisition ($f_B = 0.75$ after heat treatment and $f_B = 0.80$ before treatment). The thickness of the rigid lamellae is calculated with these numbers to be well below 5 nm ($d_A = 3.7$ nm) for the aged sample, but around 10 nm ($d_A = 11.2$ nm) before treatment. We not only observed a decrease to about 1/3 in rigid phase content by aging (see Section

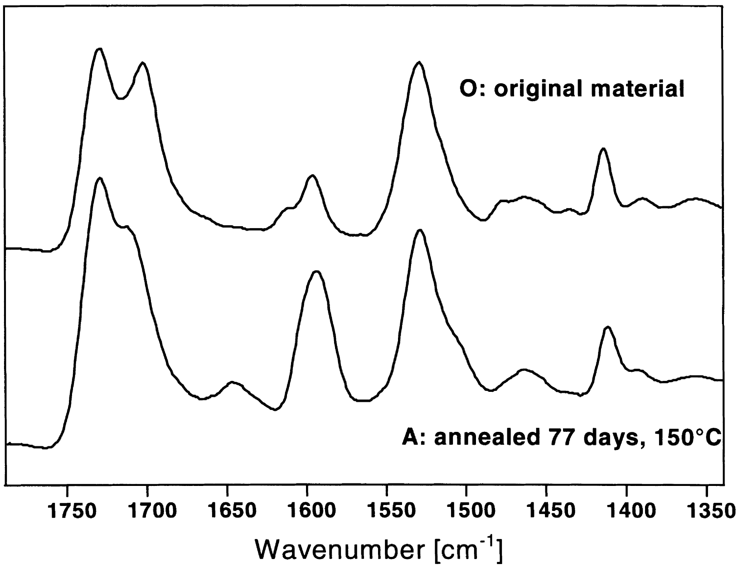

Fig. 7. IR-ATR spectra of original (top) and annealed material (bottom).

2.1.2), but also a strong decrease in the size of rigid segment domains.

Thus, we have two results regarding the phase structure of the oxidised sample: $T_{1rho}(H)$, $T_2(H)$ and the WISE indicate residual rigid domains in the aged sample with a blurred phase structure, as compared to the pristine sample where a clear-cut segregation of "rigid" and "soft" phase was found. The size of rigid domains is reduced from around 10 nm to well below 5 nm by aging.

2.2. ATR-IR spectroscopy

Attenuated total reflection infrared (ATR-IR) spectroscopy is a suitable method in order to characterise solid materials without the need to prepare the specimen in a special and sophisticated way.

Spectra presented here were recorded on a BioRad FTS 175C spectrometer with a spectral resolution of 2 cm^{-1} and a conventional DTGS detector. As measuring device we used a micro ATR unit from Harrick, the so-called split-pea®.

Fig. 7 shows a part of the ATR spectra of the original (O) and the annealed (A) material. There are several characteristic changes after thermal treatment, namely in the carbonyl (1640–1740 cm^{-1}) and the aromatic C=C stretching (1560–1620 cm^{-1}) region. Both carbonyl peaks (1730 and 1703 cm^{-1}, respectively) decrease after thermal treatment. Due to the polyester soft segment, there are at least two overlapping absorptions at 1730 cm^{-1}, originating from the ester carbonyl and the "free" (or very loosely H-bonded) urethane carbonyls. Therefore, an intensity loss of this signal due to urethane degradation is partly compensated by the non-changing ester absorption. However, associated urethane rigid segments are not only reduced in number but also there capability to form H-bonds is weakened as can be concluded from the intensity loss of the absorption at 1703 and its shift to 1711 cm^{-1}.

A closer look at the spectral region around 1650 wave numbers reveals an additional, new absorption in the *A* spectrum at 1645 cm^{-1}. This absorption is assigned to the C=O stretching vibration of a two-fold phenyl substituted ketone—namely the oxidised methylene bridge of MDI. This assignment was verified by comparison with the IR spectrum of benzophenone, which may serve as the simplest model. There, the carbonyl stretching absorption is found at 1652 cm^{-1} when measured as a potassium bromide pellet. Because of the enormous delocalisation of the π-electron pair due to the conjugation with two aromatic rings, the C=O bond loses some of its double bond character and hence, its IR absorption is shifted to lower wave numbers. Additionally, the diethyl carbamate of 4,4′-diaminobenzophenone, which may also serve as a model for oxidised MDI urethane, has its ketone absorption at 1638 cm^{-1} [20].

Another very striking change is observed for the C=C stretching vibrations at about 1600 cm^{-1}. Before the annealing process, the signal shape is an asymmetric double peak and changes to a broadened single line with increased intensity after thermal treatment. Unfortunately, we have no satisfying explanation for this finding yet. However, it at least suggests that not only the bridging methylene carbon is affected but the aromatic rings are so as well.

2.3. Hydrolysis and subsequent GC–MS

A further proof for the conversion of the MDI units to benzophenone units is provided by GC–MS. For this purpose the same polyester-TPU, aged for 77 days at 150°C in air, as used for NMR and IR investigations was hydrolysed in alkaline solution as described below. Thereby the ester and urethane bonds are cleaved. The aromatic

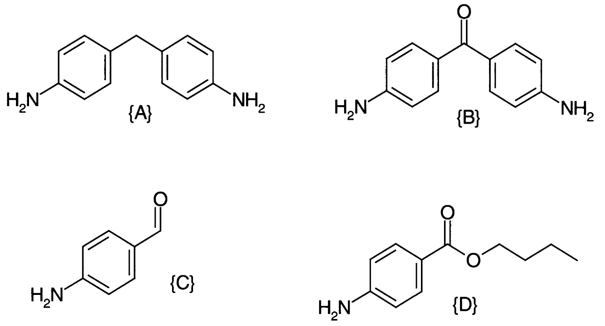

Fig. 8. Molecules detected by GC–MS after hydrolysis of the aged TPU.

urethanes are converted to aromatic diamines and diols. The polyester (Capa 223®) is hydrolysed to the ϵ-hydroxy carbonic acid salt. The diamines and diols can be extracted with an organic solvent and subsequently be analysed by GC coupled with MS. In order to quantify the products a defined amount of *N*,*N*′-tetramethyl-MDA was added to the aged TPU after hydrolysis but before extraction as an internal standard.

2.3.1. Experimental

A 100 ml flask equipped with a stirrer and a condenser was charged with 50 ml of *n*-butanol and 1.27 g of granulated aged TPU. The mixture was stirred for 2 h at 80°C under a nitrogen blanket. Then 1.5 g of KOH were added and the mixture was heated under reflux for another 2 h. Subsequently, the reaction mixture was cooled to room temperature and about 15 ml of water were added. Again, the mixture was stirred under reflux for another 3 h. Afterwards it was allowed to cool down to room temperature, neutralised with diluted HCl to pH ≈ 7 and the solvent was distilled off (50–70°C). Now, 0.1719 g of *N*,*N*′-tetramethyl MDA were added as an internal standard. The residue was extracted with ethyl acetate and washed with water. Finally, the solvent was removed from the organic extract and the residue (0.349 g) was submitted to GC–MS.

GC–MS analysis showed the presence of the substances depicted in Fig. 8: besides a small amount of non-oxidised MDA (molecular mass $M = 198$) {A}, we found a considerable amount of 4,4′-benzophenone diamine ($M = 212$) {B}. The quantification reveals, that the extract contained an amount of 4,4′-diamino benzophenone corresponding to about 35 wt%[2] of the amount of MDI used to synthesise the original TPU.

Assuming that all internal standard was transferred to the extract, only a smaller amount of amines than expected was obtained by extraction. The amount of MDA detected was smaller than an amount corresponding to 1 wt% of the original MDI used for the synthesis of the TPU. Since not all of the material was recovered by extraction and detected by GC–MS, we assume, that at least 35% of the MDI units were oxidised.

Also small amounts of 4-amino benzaldehyde {C} and 4-amino *n*-butlybenzoate[3] {D} were found, which can be explained, according to Wilhelm et al. as products resulting from a direct decompositon of the MDI hydroperoxide.

3. Discussion

The major question investigated in the previous chapters is, whether the oxidation of the soft phase alone is responsible for the aging of TPU or whether there also is, contribution from the rigid phase. In order to simplify the spectrum of oxidation products, polyester based TPU was examined, since polyesters are less prone to oxidation than polyethers. The oxidation products formed upon aging of polyester based TPU for 77 days at 150°C in air, were investigated by solid state NMR, IR and GC–MS.

The results of all three methods support our hypothesis (see Fig. 9), that the MDI unit is oxidised at its central methylene group. Proof for the formation of this benzophenone derivative are a resonance at 194 ppm detected by CP/MAS NMR, a carbonyl stretching vibration at 1645 cm^{-1} detected by IR and the benzophenone diamine (molecular mass: 212) found by GC–MS after hydrolysis of the aged TPU. The amount of the benzophenone derivative formed after aging for 77 days can be estimated to be more than 35% by GC and approximately 50% by NMR. Additionally, it was found by ^{1}H relaxation experiments, that upon aging the content of rigid phase decreases to only 5% corresponding to one-third of the initial amount of rigid phase. Besides, also the size of the rigid domains drops to about one-third of its initial value. Simultaneously, the NMR-glass temperature of the polyester-TPU rises by nearly 50°C and spin diffusion experiments reveal that a blurred phase structure results. Our interpretation is that the polyurethane segments containing oxidised MDI units mix better with the soft phase than the non-oxidised derivatives. Interestingly enough, the signal intensity of urethane groups is found to be the same before and after aging. This indicates that the urethane bonds are hardly destroyed by aging. The urethane groups as well as the polyester blocks remain more or less unaffected, confirming—as initially stated—that the failure is caused by the rigid phase.

The results show, that the methylene group in MDI based TPU is oxidised upon aging in air at 150°C. After 77 days quite a large amount (35–50%) of the MDI units are oxidised.

Benzophenone formation upon oxidation of the diethyl urethane of MDI was already observed by Schultze [19] and Skorich et al. [20]. Furthermore, Allen et al. [21] found benzophenone impurities in phosphorescence

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[2] Sensitivity factors of *N*,*N*′-tetramethyl MDA and 4,4′-diamino benzophenone for MS were neglected.

[3] The *n*-butanol derivative results from the hydrolysis using *n*-butanol as additional solvent.

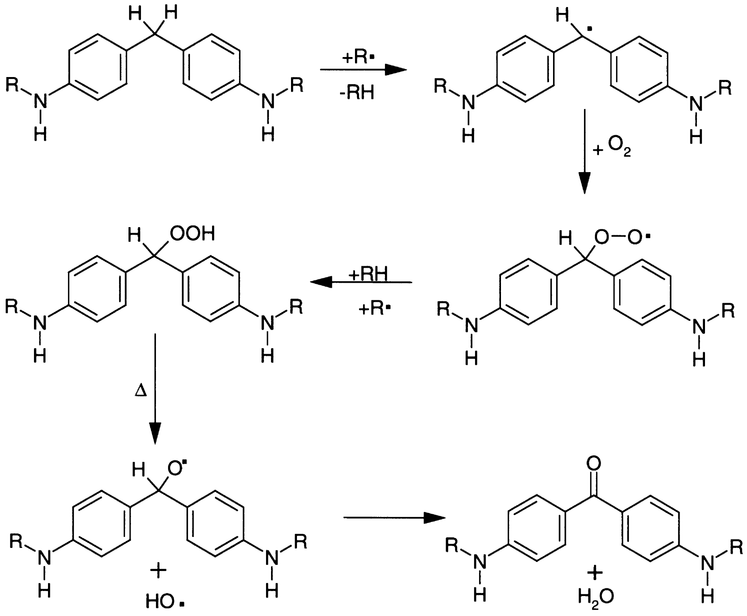

Fig. 9. Supposed path of oxidation of the MDI unit.

spectra of TPU. They supposed that this impurity was a result of oxidation of the methylene group of MDI and may have been formed at some stage of polymer manufacturing.

In this work it could be proved, that even in thermoplastic polyurethanes, the MDI unit is oxidised to a benzophenone derivative upon thermal aging in air. This affects the phase structure and rigid phase content of the TPU, explaining the commonly observed decrease in hardness and worsening of mechanical properties. Obviously, the oxidation of the MDI unit causes a decrease in rigid phase content and a blurring of the phases, which might be due to enhanced solubility of oxidised “rigid” blocks in the soft phase.

4. Conclusions

Our investigations by solid state NMR, IR-ATR and GC–MS show that benzophenone derivatives are formed upon aging TPU at 150°C in air. The MDI methylene unit is obviously converted into a benzophenone structure upon oxidation. After aging for 77 days between 35 and 50% of the total MDI units are found to be oxidised.

Simultaneously, the amount of rigid phase diminishes. According to solid state NMR results, only about one-third of rigid phase persists. Additionally, an increase in glass transition temperature of about 50°C is observed after the same period of aging. To explain this, a mixing of oxidised “rigid” segments with the soft segments is supposed. The urethane groups on the other side are hardly affected.

The above-mentioned results show that besides thermal oxidation of the polyether segments oxidation of the rigid block contributes to the chemical aging of TPU. Namely, oxidation of MDI units leads to the disintegration of the rigid phase. The rigid phase serves as a physical crosslink, which is necessary to achieve elastic recovery of the material. Therefore, with the loss of the rigid phase the elastic properties worsen.

These investigations on thermal aging of TPU show that besides the polyether segments also the MDI-structure in TPU is another weak point in the polymer structure in thermal aging of thermoplastic polyurethane. Therefore, the aging of TPU can be retarded by the right choice of raw materials.

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References

[1] Wilhelm C, Gardette JL. Polymer 1998;39(24):5973–80.
[2] Mathur GN, Kresta JE. Polym Sci Technol 1984;26:135–53.
[3] Marchal J. Journal Bureau of Standards Special Publication 357. The mechanism of pyrolysis, oxidation, and burning of organic materials. Proceedings of the Fourth Marterials Research Symposium, 26–29 October 1972. p. 85–94.
[4] Thomassin C, Marchal J. Makromol Chem 1977;178:981–1003.
[5] Thomassin C, Marchal J. Makromol Chem 1977;178:1295–312.
[6] Thomassin C, Marchal J. Makromol Chem 1977;178:1313–25.
[7] Thomassin C, Marchal J. Makromol Chem 1977;178:1327–39.
[8] Davis A, Golden JH. Makromol Chem 1965;81:38–50.
[9] Dreyfuss P. Poly(tetrahydrofuran). Polymer monographs, 8. New York: Gordon and Breach Science, 1982. p. 174–9.

[10] Wilhelm C, Rivaton A, Gardette JL. Polymer 1998;39(5):1223–32.
[11] Gardette JL, Lemaire J. Makromol Chem 1982;183:2415–25.
[12] Gardette JL, Lemaire J. Makromol Chem 1981;182:2723–36.
[13] Komoroski RA, editor. High resolution NMR spectroscopy of synthetic polymers in bulk, Deerfield Beach: VCH, 1986 chaps. 1, 3 and 4.
[14] Schmidt-Rohr K, Clauss J, Spiess HW. Macromolecules 1992;25(12):3273–7.
[15] Schmidt-Rohr K, Spiess HW. Multidimensional solid-state NMR and polymers, London: Academic Press, 1994 chaps. 6 and 13.
[16] Aujla RS, Harris RK, Packer J, Parameswaran M, Say BJ, Bunn A, Cudby MEA. Polym Bull 1982;8:253–9.
[17] Asano A, Takegoshi K. Polymer blends and miscibility. In: Ando I, Asakura T, editors. Solid state NMR of polymers, Amsterdam: Elsevier, 1998 chap. 10.
[18] Egger N, Schmidt-Rohr K, Blümich B, Domke WD, Stapp B. J Appl Polym Sci 1992;44(2):289–96.
[19] Schultze H. Makromol Chem 1973;172:57–75.
[20] Skorich SR, Benz ME. Polym Mater Sci Eng 1998;79:506–7.
[21] Allen NS, McKellar JF. J Appl Polym Sci 1976;20:1441–7.