

NMR · Relaxation time · Polyurethane coating · Artificial aging

$^1\text{H-NMR}$ transversal relaxation measurements have been successfully applied for determination of T_2 in three types of model polyurethane coatings. The emphasis was given on the comparison of the cross-linking state before and after artificial exposure. Temperature dependence of T_2 for differently cross-linked polyester-polyurethane systems has also been measured. Results show a clear dependence of NMR parameters on polyurethane cross-linking and aging. Additionally, industrial coatings at five different grades of cross-linking have been examined.

Untersuchung des Einflusses von oxidativen Alterungsprozessen und dem Effekt von Lichtschutz-Stabilisatoren auf die Vernetzungsdichte von Polyurethan-Lacken mittels $^1\text{H-NMR}$ Relaxationszeit-Messungen

NMR · Relaxationszeit · Polyurethan-Lacke · künstliche Alterung

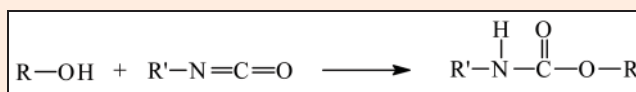
Transversale $^1\text{H-NMR}$ Relaxationsuntersuchungen wurden erfolgreich zur Charakterisierung der Vernetzungsdichte von Alterungsprozessen an drei unterschiedlichen Typen von Polyurethan-Lacken eingesetzt. Der Schwerpunkt der Untersuchungen liegt dabei auf dem Vergleich des Vernetzungszustandes vor und nach der Exposition der Proben bei unterschiedlichen klimatischen Bedingungen. Die Abhängigkeit der T_2 -Zeiten von der Meßtemperatur und den Alterungsfaktoren wurde ebenfalls untersucht. Die Ergebnisse zeigen eine eindeutige Abhängigkeit der NMR-Parameter von der PUR-Behandlung und den Alterungsbedingungen sowie deren Eignung zur Charakterisierung der Vernetzungsdichte.

$^1\text{H-NMR}$ Relaxation Study of Cross-Linking and Aging Processes in Polyurethane Coatings

Several papers have proven that the measurement of the transversal $^1\text{H-NMR}$ relaxation is a successful method for the investigation of structural and dynamic parameters in polymer networks [1–8]. This method was originally developed for elastomers and is applied here to polyurethane coatings [4].

Automotive interior coatings are mostly two-component polyurethanes, the polyol component being commonly based on polyester and polyacrylic resins. Particularly soft coatings usually have a soft, leather-like feel and provide surfaces with improved haptic, acoustical and optical properties. Polyurethane network is a result of chemical reaction between an isocyanate functionality with hydroxyl groups, as shown in Scheme 1. A stoichiometric excess of isocyanate can encourage formation of biuret and allophanate. This will result in an increase in the level of hard segments in the polymer structure and extensive cross-linking of the polymer network. The hard-to-soft segment ratio and the degree of cross-linking is a critical parameter in determining the final properties of the polyurethane polymer.

tional averaging depends on the local dynamics and on the constraints of the hydrocarbon chains imposed by network junctions and topological restraints. In contrast to the isotropic tumbling of small molecules, the fast local motions of network chains (typical rotational correlation times $\tau_r = 10^{-7}$ s) fixed at both ends by permanent cross-links are inherently anisotropic and, therefore, cannot average out the static dipolar interaction to zero. A small fraction q of the second moment M_2 of this interaction is left, which can be measured and correlates to the dynamics of the cross-linked hydrocarbon chain segments. The overall motion of the whole network segment is assumed to as isotropic tumbling with a much slower correlation time τ_s ($\tau_s = 10^{-3}$ s). The fast motion of chain ends is considered to be near isotropic ($q = 0$) with a correlation time τ_r . Following this dynamic model, the decay of the transversal magnetization of a polymer network is a superposition of at least three components, describing the signal decay arising from network chain segments, dangling chain ends, and small molecules such as remaining monomer units, solvent or other



Scheme 1
Formation and structure of urethane

Theory

$^1\text{H-NMR}$ Relaxation is caused by inter- and intramolecular dipolar magnetic interactions of protons, and contains information about the motional averaging of the dipolar interactions between nuclei of the hydrogen atoms. In polymer networks at temperatures above the glass transition temperature, this interaction is averaged by the thermal molecular motion of the hydrogen atoms within the hydrocarbon backbone of the network. The extent of mo-

Autoren

M. Fratricova, P. Schwarzer, Wolfsburg, W. Kuhn, Blieskastel

Corresponding author:
Dr. Winfried Kuhn
IIC Innovative Imaging Corp. KG
Talstr. 88
66440 Blieskastel
Tel. +49 68 42/9 60-3 10
Fax: +49 68 42/9 60-3 20
e-mail: wpk01@iic-nmr.com

uncross-linked molecules, respectively. Under these assumptions, the total transversal magnetization decay has been derived to [6–8]

$$M(t) = A \exp\left(-\frac{t}{T_2} - \frac{qM_2 t^2}{2}\right) + B \exp\left(-\frac{t}{T_2}\right) \quad (1)$$

The relaxation function (1) is a composition of a Gauss-like and an exponential part. The relaxation process for the fast moving and nearly isotropic tumbling dangling chain ends and small molecules can be described by the pure exponential fraction due to a simple exponential BPP-like correlation function [9], while the anisotropic movement of the network and intercross-link hydrocarbon chains leads to the gauss-like fraction of the relaxation function [6–8, 10]. The parameters A and B are the fractions of magnetization (equivalent to the mass fraction) of the intercross-link chains and the dangling chain ends, respectively. The residual static dipolar interaction qM_2 is at temperatures well above the glass transition temperature of pure intramolecular nature. At such temperatures, intermolecular interactions can be neglected. While the transverse magnetization decay in a variety of sulfur cured technical rubbers is very well described by the relaxation function (1) the gauss-like fraction of the magnetization decay can not be observed in polyurethane coating systems, similar to EPDM elastomers and epoxy resins [11, 12]. The reason may be the very short

relaxation time T_2 of coating systems, even at elevated temperatures. Instead, a mono (2) or bi-exponential magnetization decay can be observed (3), consisting of an exponential function describing a short relaxation time T_{21} , assigned to the cross-linked network, and a comparable long relaxation time T_{22} representing the highly mobile free dangling chain ends.

$$M(t) = A_t \exp(-t/T_2) \quad (2)$$

$$M(t) = A_1 \exp(-t/T_{21}) + A_2 \exp(-t/T_{22}) \quad (3)$$

The coefficients A_1 and A_2 represent the relative (observable) amount of cross-linked molecules and freely movable molecules and chain ends.

Objective of the present study is the application of this method for polyurethane coating systems and investigation of the cross-linking state by means of ^1H transverse relaxation time T_2 .

Experimental

Materials

Three types of model polyurethane (PUR) coatings were studied. They were two-component, solvent-based films prepared from three various types of polyol (polyester, polyether and polyacrylate – short description is given in Table 1) and one type of hardener (aliphatic polyisocyanate based on HDI, NCO content 16.5%) in the ratio NCO/OH = 1.2 as commonly used in the coating technology. Three types of light sta-

bilizers were used – HALS (Tinuvin T292, Ciba Specialty Chemicals), UV absorber (UVA, Tinuvin T1130, Ciba Specialty Chemicals) and antioxidant (AOX, Hostanox O3, Clariant). The amount of added catalyst was 0.5 wt% of the amount of resin. Black pigment paste consisting of 50 wt% carbon black and 50 wt% solvent was added at 10% to the resin. The amount of additives added to the resin is given in Table 2. The films were applied at a 60 μm thickness on glass plates and cured at 80°C for two hours, and then for 24 hours at room temperature. An industrial coating of unknown composition, but at five different ratios of NCO/OH (0.75, 0.85, 1, 1.15 and 1.25) was provided by a coating supplier. Model coatings with other ratios NCO/OH have also been prepared, as given in Figure 6.

NMR instrumentation

NMR measurements were carried out using the IIC MR-CDS 3500 cross-link density spectrometer at a magnetic field strength of 0.35 Tesla, corresponding to 15 MHz proton resonance frequency. A Hahn-Echo pulse sequence was applied with a 90° pulse duration of 1.8 μs and a 180° pulse of 3.8 μs . 64 time domain signals were acquired at spin-echo times τ between $\mu\text{s} \leq \tau \leq 2.5$ ms. The measurements were carried out at a temperature of 120°C. A nonlinear Marquardt-Levenberg-algorithm has been used for data analysis using the dedicated software package IIC-Analysis, based on IGOR® Pro, Wavemetrics, Lake Oswego, Oregon, USA.

Using time domain signals, data analysis was performed based on a mono- (4) or bi-exponential expression (5), respectively:

$$M(t) = A_0 + A_1 \exp(-t/T_2) \quad (4)$$

$$M(t) = A_0 + A_1 \exp(-t/T_{21}) + A_2 \exp(-t/T_{22}) \quad (5)$$

with A_0 as an additive constant to compensate for dc offsets with no physical meaning.

The results of a typical data analysis are given in Fig. 1.

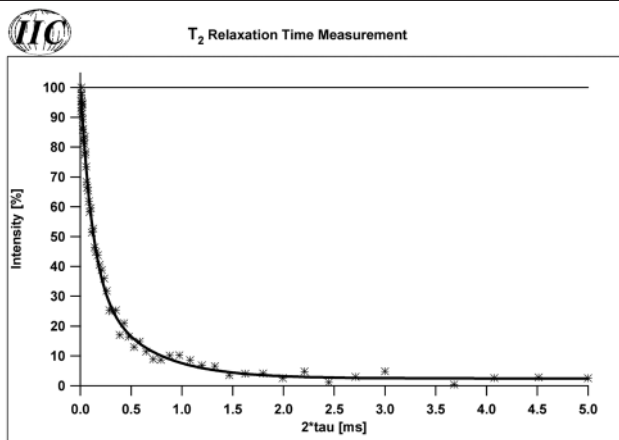
Weathering conditions

The samples were exposed to an artificial weathering instrument Xenotest Beta LM (Atlas, Germany) for various numbers of periods, period being a specified dose of irradiance defined by DIN 75202. Five periods simulate one year of weathering under hot-dry conditions. The device was equipped with xenon lamps and operated at following conditions: cut-off of the simulated so-

Name	Form of supply	Acid value	Viscosity (23°C)	Content of alkali	Content of water	Density (20°C)	
		[mg KOH/g]	[mPa × s]	[%]	[%]	[g/ml]	
ACR	polyacrylate based polyol	75% in Xylol	5 ± 2	3500 ± 500	2.8 ± 0.2	≤ 0.1	1.06
EST	polyester based polyol	solvent-free	≤ 2,5	2200 ± 400	4.3 ± 0.4	≤ 0.1	1.17
ETH	polyether based polyol	solvent-free	≤ 1	5000–7000	27	≤ 0.2	–

None	HALS	UVA	AOX	HALS + UVA	HALS + AOX	AOX + UVA	HALS + UVA + AOX
	1.0	1.0	1.0	0.7	1.0	1.0	0.7
				0.3	1.0	1.0	0.3
							1.0

1



T₂ Bi-Exponential Data Analysis

Auftrags-Nr: W75X1 Prüf-NR.: W75X1
 Comment: VW PUR
 Rubber: PUR Polyurethane

T₂₁ = (0.11 ± 0.01) ms AT₂₁ = 65.50 %
 Var. Coeff. = ±11.15 %
 T₂₂ = (0.52 ± 0.11) ms AT₂₂ = 34.51 %
 Var. Coeff. = ±21.09 %

M(00) = 2.42 %
 SDEV = 270.95
 SNR = 89.18
 Mass Density Rho = 0.950 g/cm³

NMR Data File: W75X1.DAT
 Date: Sa, 10. Sep 2005, Time: 22:27:55

IIC Innovative Imaging Corp. KG
 MR-CDS 3500

NMR Measurement Parameters:
 Method : XLD
 FID Data Points : 255
 Dwell Time : 20 us
 Gain : 55 dB
 Number of Expt's : 64
 Number of Acq's : 10
 T_i : 120
 T_e : 120
 T_{avg} : 120

1 Example of bi-exponential data analysis

lar radiation at 320 nm, 60 W/m² irradiance in spectral range 280–400 nm, 65°C sample-space temperature and 100°C black standard temperature.

Sample preparation

The samples were scratched from the glass with the help of scalpel. The coating films were put into the glass tubes and placed into the magnet field of the spectrometer.

Universal hardness instrumentation

Universal hardness measurements were carried out using Fischerscope Hardness Control unit (HCU). Universal hardness (HU) is defined by DIN 50359 and is given in N/mm².

Results and discussion

Figure 2 shows the development of the magnetization decay at 64 different timings for the three various types of polyurethane coatings. In comparison to the plots of technical rubbers, the spin-spin relaxation time T₂₁ of polyurethane coatings (~ 100 μs) is

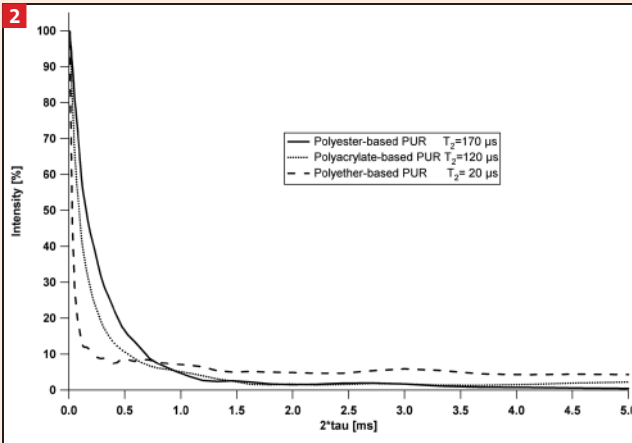
substantially shorter than for technical rubbers (~ 10 ms) [11]. This is a consequence of different molecular dynamics in both systems. T₂₂ corresponds to the highly mobile fraction of the network (dangling chain ends or solvent molecules) and is a measure of the cross-linking and hence tightness of the system.

Universal hardness of three various polyurethane systems was also measured. The hardest polyurethane coating was the polyether-based PUR (142 N/mm²), followed by polyacrylate- (92 N/mm²) and polyester-based PUR (38 N/mm²). The corresponding T₂ values are 20, 120 and 170 μs. There is an obvious relationship between hardness of polyurethane and the transversal relaxation time T₂. The hardness is among other factors also a consequence of the number of chemical crosslinks among polyisocyanates and polyols (indirectly by OH-number of polyols, see Table 1) and junctions. The molecular mobility, reflected by T₂, depends on the mixture of crosslinks and junctions. The smaller the T₂ value, the lower the degree of freedom of the molecular motion and the more rigid the network.

Investigation of ageing processes in model polyurethane coatings

Three various polyurethane systems with three various light-stabilizers (in eight possible combinations as given in Table 2) have been investigated. The temperature of the measuring cell was 100 °C. T₂ values have been obtained for unexposed, and in Xenotest Beta LM exposed samples, respectively. The maximum extent of exposure, e.g. 9 periods, simulates approximately 2 years of weathering in desert (Kalahari/Phoenix). As for polyester-based PUR, the influence of the artificial ageing can be observed. After 9 periods in Xenotest, the presence of light-stabilizers shortens the relaxation from 280 μs (for un-stabilized samples) to smaller values. 150 μs is the smallest T₂ value obtained, which means that the combination of all three stabilizers has the maximal protection impact for this system. Unexposed samples have similar T₂, in interval 150–160 μs, influence of light stabilizers is neg-

2



2 Plot of envelopes of magnetization decays at 64 different timings for three different model polyurethane coatings (on the base of polyether-, polyester- and polyacrylate)

3 T_2 values of differently stabilized samples for poly(ester-polyurethane), unexposed and after 9 periods exposure in Xenotest weathering device

EST	none	HALS	UVA	AOX	HALS + UVA	HALS + AOX	UVA + AOX	All
0×	160	150	160	150	150	140	150	160
9×	280	170	190	190	160	150	190	150

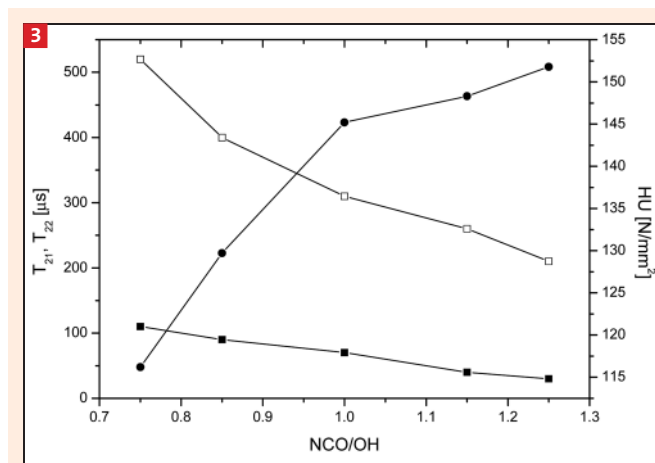
ligible and fluctuation is caused by the deviation of measurement (Table 3).

T_2 values for polyacrylate-based polyurethane have not changed to such an extent as in the case of polyester-based PUR. After 9 periods in Xenotest, the distribution of the T_2 values in the range 120–130 μs is similar to that obtained for the unexposed stabilized samples. This means that the polymer network is not being degraded by UV-exposure and thus the stabilized polyacrylate-based PUR shows the highest weathering stability of all polyurethane types. The situation is different for unstabilized and with UVA stabilized samples, respectively. For these systems, T_2 changed from 120 to 170 μs , and thus the protection impact of this type of stabilizers is not sufficient enough to prevent the degradation of the polyurethane matrix.

In the case of polyether-based PUR, after 9 periods of exposure in Xenotest device, T_2 values have increased from 20 μs (unexposed samples) to a range of values between 40–80 μs for the differently stabilized exposed samples. The highest T_2 value (80 μs) was obtained for un-stabilized ETH-PUR; the lowest for the combination of following stabilizers – HALS, HALS + AOX, HALS + UVA and the combination of all three stabilizer (HALS + AOX + UVA). These results reveal that the presence of HALS is crucial for the photo-oxidation stability of this system. T_2 values are generally low for polyether-based polyurethane. Because of its hardness and consequently rapid transversal relaxation, the cross-link density spectrometer is here at its capability limits. Polyester- and polyether-based PUR containing black pigments are in general giving lower T_2 values. This can be observed for both, unexposed and exposed samples. In contrary to these findings, the presence of black pigment in polyacrylate-based PUR does not affect T_2 for this type of polymer.

Investigation of degree of cross-linking in industrial polyurethane coatings

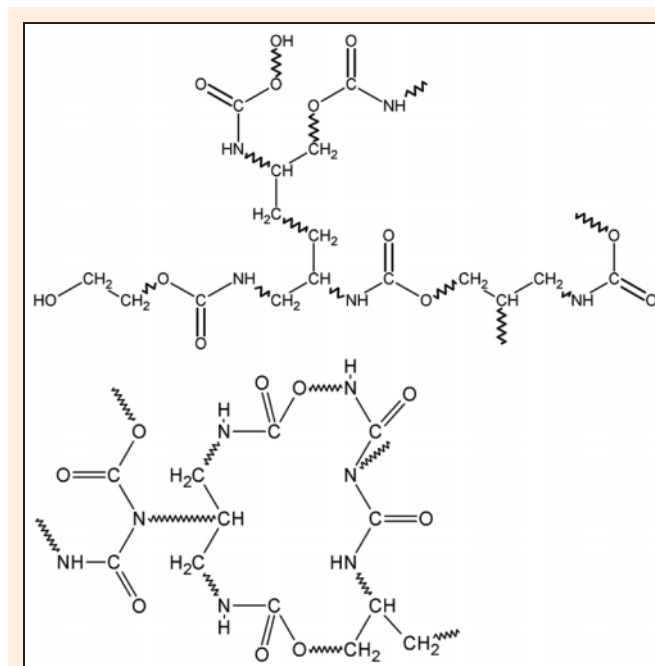
Both, mechanical and NMR T_2 measurements show a clear dependence on the ratio of NCO/OH (Fig. 3). An excellent correlation between the hardness parameters and the decrease of T_2 relaxation times could also



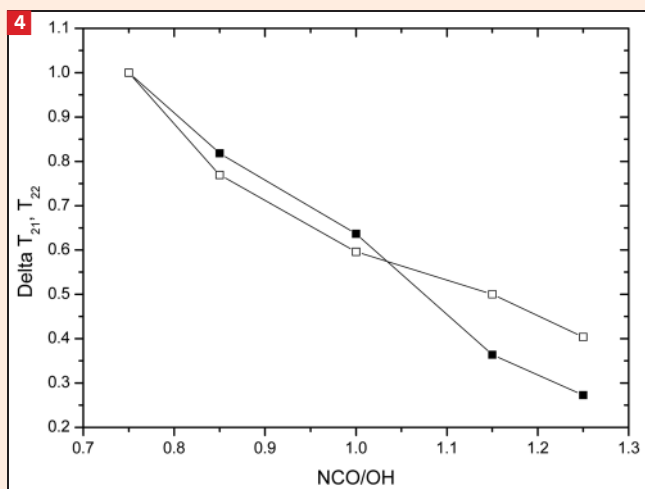
3 Decrease of the mobility of the polyurethane network molecules T_{21} (■) and T_{22} (□) with the increasing NCO/OH ratio

be observed. An interpretation of the two component NMR data analysis is based on the models of the chemical structure of cross-linked polyurethane depending on the NCO/OH ratio (Scheme 2a and 2b). For NCO/OH < 1, the type of molecular motion is mainly determined by the long chain and branched hydrocarbon backbone with its high degree of molecular mobility, characterized by the long relaxation time T_{22} be-

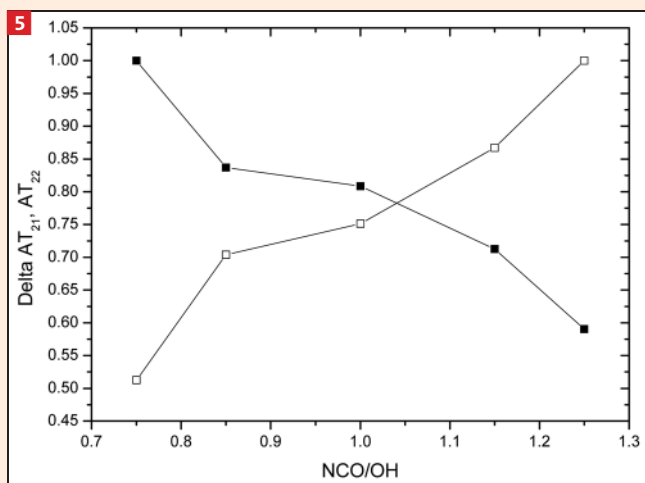
tween 370 μs and 630 μs . A fast relaxing component with T_{21} between 60 μs and 110 μs can also be observed, resulting from some immobilized branched parts of the molecule. With increasing NCO/OH ratio, the number of cross-links is also increasing, leading to a progressive increase of hardness (Fig. 3) and a significant decrease of T_2 . Figure 4 indicates a stronger decrease of T_{22} up to an NCO/OH ratio of 1, may be



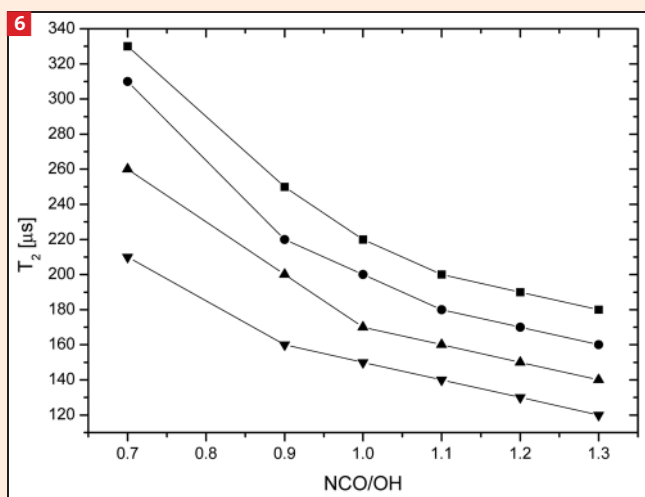
Scheme 2 Structure of polyurethane with the amount of functional groups NCO < OH (a) and NCO ≥ OH (b), where wavy lines represent branched hydrocarbon chains according to the used polyol resin



4 Change of molecular mobility of the polyurethane network ΔT_{21} (■) and ΔT_{22} (□) with the increasing NCO/OH ratio



5 Development of relative amounts of differently mobile molecules ΔT_{21} (■) and ΔT_{22} (□) of the polyurethane network with increasing NCO/OH ratio



6 Dependence of transversal relaxation time T_2 on cross-linking of the system (ratio hardener to polyol) at four different temperatures 80 °C (▲), 90 °C (△), 100 °C (◆) and 120 °C (■) for polyester-based polyurethane T_2

increases now much stronger, while the mobility of the hydrocarbon chains connecting the network structures with each other remains and is not affected in the same way. The crossing point of the decrease of molecular dynamics, indicated by the change of decrease of T_2 , appears at the NCO/OH ratio of approximately 1 (Fig. 4). The plots shown in Figure 5 are the corresponding relative ratios of the amount of slow (AT_{21}) and fast (AT_{22}) moving fractions of the entire molecule. Both adding up to 100%, whatever there real amount in the polymer is. It might be difficult to understand, that the amount of highly immobilized network seems to be decreasing with increasing NCO/OH ratio, but the explanation may be the visibility of immobilized polymer by NMR methods. Rigid fractions of the network become invisible and consequently can not be detected by NMR T_2 measurements, if there T_2 falls below a value less than the shortest τ -value in the τ -list of the experimental parameters. The shortest τ -value used in the measurement parameters is determined by the hardware of the spectrometer, in this case by the ring-down delay of the radiofrequency coil of approximately 10 μ s.

Temperature dependence of T_2 for differently cross-linked polyester-PUR systems

Transversal relaxation times T_2 for six differently cross-linked polyester-based polyurethanes have been measured at four temperatures. The results are shown in Figure 6. These measurements show that at an arbitrary temperature, the greater the number of cross-links in the polyurethane systems, the smaller the value of T_2 . This is in accordance with the assumption, that the decreasing motional degree of freedom reduces T_2 values. Consequently, T_2 values are increasing with increasing temperature due to the higher mobility of the network. Referring to Schemes 2a and 2b, a rough estimation of the activation energies for different types of molecular motion can be obtained analyzing the temperature dependence of T_2 . Assuming an activation energy of 42 KJ/mol for crankshaft motions of linear polymer chains [12], as the hydrocarbon backbone of amorphous polyurethane for the ratio of NCO/OH < 1 may be considered, the activation energy for the tumbling polymer network segment can be roughly estimated using the Arrhenius approach $R = 1/T_2 \sim \tau_c = \tau_{c0} \exp(-E_A/kT)$ with τ_c equal the molecular rotational correlation time.

because of the stronger immobilization of highly mobile components of the network and a formation of cross-links between the hydrocarbon backbone, while the already slowly moving parts of the molecule are not affected in the same manner. For

the ratio NCO/OH > 1, the molecular mobility seems to be dominated by the highly cross-linked part of the polymer, corresponding to a T_{21} approximately 70 μ s and less, and T_{22} values below 400 μ s. The mobility of the slow-moving network de-

This will be in detail discussed in a following paper.

Conclusions

Polyurethane coatings were subjected to the ^1H -NMR relaxation study. The degradation of the polymer network after artificial weathering was observed as a prolongation of the relaxation time T_2 . The reason for longer T_2 times is the deterioration of the network into fractions of higher molecular mobility. The protection impact of the stabilizers was evaluated by comparison of unexposed and in Xenotest exposed samples. The results also proved that the network of poly(acrylic-urethanes) is resistant against weathering. The protection impact of the black pigment is relevant just for the unstabilized samples; the presence of any of used stabilizer turns its impact negligible. An excellent correlation between hardness and T_2 relaxation times of polyurethanes could be observed. The mobility of the differently crosslinked polyurethane network was characterized by the relaxation times T_{21} and T_{22} , and a model explaining the ob-

served relaxation behavior has been introduced. Faster relaxation of the system with the NCO/OH ratio < 1 can be explained by the presence of dangling chain ends. These free moving parts of molecules are completely missing for the NCO/OH > 1 maybe due to crosslinking of isocyanate components to allophanate and urea bridges. It was also shown that the T_2 values increase with increasing temperature due to the higher mobility of the network. The results indicate that ^1H -NMR relaxation techniques can be effectively used as a tool for characterization of crosslinking as well as for observation of aging processes in the polyurethane coatings matrix.

Acknowledgement

The authors would like to thank Carla Hoepfner and Dr. Heinz-Wilhelm Wilde (company Mankiewicz GmbH) for valuable discussions and supply of the samples. Special thanks to Timo Tolksdorf for introduction to NMR equipment as well as to Marcus Grau who helped to carry out the experiments (both Volkswagen AG).

References

- [1] Y.Y. Gotlib, M.J. Lifschitz, V.A. Sevelev, J.S. Lisanski and J.V. Balanina, *Vysokomol. Soedin. A* **10** (1976) XXVII 2299.
- [2] V.D. Fedotov, V.M. Cernov and T.N. Khasanovic, *Vysokomol. Soedin. A* **4** (1978) XX 919.
- [3] A.D. English, *Macromolecules* **18** (1985) 178.
- [4] G. Simon, H. Schneider and K.G. Häusler, *Prog. Colloid Polym. Sci.* **78** (1988) 30.
- [5] M.G. Brereton, *Macromolecules* **23** (1990) 1119.
- [6] W. Gronski, U. Homann, G. Simon, A. Wutzler and E. Straube, *Rubber Chem. Technol.* **65** (1992) 63.
- [7] G. Simon, K. Baumann and W. Gronski, *Macromolecules* **25** (1992) 3624.
- [8] W. Kuhn, P. Barth, S. Hafner, G. Simon and H. Schneider, *Macromolecules* **27** (1994) 5773.
- [9] N. Bloembergen, E.M. Purcell and R.V. Pound, *Phys. Rev.* **73** (1948) 679.
- [10] P.W. Anderson and P.R. Weiss, *Rev. Mod. Phys.* **25** (1953) 269.
- [11] W. Kuhn and S. Kelbch, *Crosslink Density International Rubber Conf., IRC 2000 Proc. Helsinki, Finland*, 12.–15. 6. 2000, 119.
- [12] R.H. Boyd and S.M. Breitling, *Macromolecules* **7** (1974) 855.