

Solid-State NMR Studies of Relaxations in Modified Duroplastic Low-Stress Materials

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SYNOPSIS

Duroplastic low-stress molding materials, based on epoxy novolak resins with different siloxane modifications have been investigated with respect to the mobility of different structural elements and the morphology of the resulting polymers. Different solid-state NMR relaxation experiments have been used to probe the mobility in a wide range of motional frequencies. Spin diffusion experiments allowed the estimation of domain sizes even in the case of highly filled polymers and indicate that the effect of low-stress modification is correlated with microphase separation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Today's state-of-the-art duroplastic encapsulating materials for large-scale integrated circuits are based on filled epoxy-novolak-systems that are characterized by high Young's moduli and glass transition temperatures and low thermal expansion coefficients; this triangle of macroscopic properties determines in a first approximation the internal stress in the molding material.¹ Especially in a microchip with its variety of different materials with different thermal and elastic properties, a temperature-dependent buildup of stresses is almost unavoidable and can lead to severe interferences in the chip function. Material development for further chip generations with increasing chip size and decreasing pattern size² has to take this into account.

On a molecular level, these stresses are influenced by structure, network density, and relaxation behavior of the polymer as well as morphological characteristics of the molding material. Solid-state NMR is well suited for an investigation of such "microscopic" material properties, as it offers the possibility for structural characterization and also gives profound information on dynamics and morphology.

NMR relaxation times, in general, are affected by several effects,³ e.g., dipole-dipole interaction,

spin-rotation relaxation, chemical shift anisotropy, scalar coupling, and interaction with paramagnetic compounds. The most important mechanism for longitudinal relaxations in macromolecules is the dipole-dipole interaction, which is strongly influenced by motions in the corresponding frequency range. In the case of the "extreme narrowing limit," in general, an increasing mobility of structural elements corresponds to an increase in longitudinal relaxation times.^{3,4}

With different relaxation experiments motions in a wide frequency range can be detected:⁵

1. Spin-lattice relaxation times (T_1) are modulated by motions with frequencies in the MHz region.
2. In the mid-kHz range it is the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), which is sensitive to motions in this frequency range.⁶ It is measured by a variation of the spin-lock time of the corresponding nucleus in the crosspolarization (CP) experiment.
3. Slow motions (about 10^2 Hz) can be detected by measuring the rate of magnetization transfer from ^1H to ^{13}C ($1/T_{\text{CH}}$) in the CP experiment. It has been shown, that T_{CH} -times can be correlated with mechanical relaxations.^{7,8}
4. The detection of even slower motions with a one-dimensional (1D) mixing-time experiment⁹ has the advantage of an exact fre-

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quency assignment. It uses the rebuild of previously suppressed spinning sidebands caused by structural motions.

Information on morphology is gained from two types of experiments:

1. For a qualitative morphological characterization the ^1H -spin-lattice relaxation time in the rotating frame, $T_{1\rho}(^1\text{H})$, is suitable.⁶ Fast spin-spin interactions (spin diffusion) among the hydrogens results in a unique $T_{1\rho}(^1\text{H})$ time. These interactions are disturbed by phase boundaries, so that systems with two or more phases show several $T_{1\rho}(^1\text{H})$ relaxation times.
2. With the new 2D- ^1H - ^{13}C wideline separation (WISE) solid-state NMR experiment, the spin diffusion process can be observed quantitatively. The wide ^1H -NMR lines can spread out according to the chemical shifts of corresponding ^{13}C -nuclei, and changes due to spin diffusion can be detected. As the spin diffusion is governed also by morphology, this experiment offers a possibility to estimate phase/domain sizes with the solid-state NMR.^{10,11} The aim of this contribution is the characterization of the structural mobility and the morphology of newly modified molding materials.

EXPERIMENTAL

Solid-State NMR

Solid-state NMR experiments were carried out on a Bruker AC 300 spectrometer operating at a 75.43

MHz carbon frequency with a narrow bore CP/MAS probehead.

A 90° -pulse length was about $4.5 \mu\text{s}$ and crosspolarization time was 1 ms. Samples were spun in ceramic rotors with a magic angle spinning (MAS) frequency of 2.5 kHz. To eliminate spinning sidebands and ^{13}C - ^1H -dipolar coupling, the TOSS-sequence¹² and high-power dipolar decoupling during ^{13}C -detection was used, respectively. The decoupling frequency was in the range of 50 to 60 kHz. All chemical shifts are given relative to tetramethylsilane.

$T_{1\rho}$ relaxation times were measured by a variation of the spin-lock time of the corresponding nucleus during the CP-experiment according to Schaefer et al.¹³

Figure 1 shows the pulse scheme of the 2D-WISE experiment. After the first 90° - ^1H pulse, which creates magnetization in the x,y plane, evolution takes place during t_1 . The second pulse brings the magnetization back into the z direction and the mixing time t_m starts. During t_m , spin diffusion takes place. The mixing time is followed by a "normal" CP-experiment with 90° - ^1H -pulse, the magnetisation transfer ^1H - ^{13}C , the TOSS-sequence, and the ^{13}C detection with ^1H decoupling.

Materials

Molding materials are, in general, made from an epoxy component and an OH group-containing component (the hardener). The materials under investigation were synthesized using two slightly different epoxy components (modified Bisphenol-A diglycidylethers, BADGE) and three different novolak hardeners:

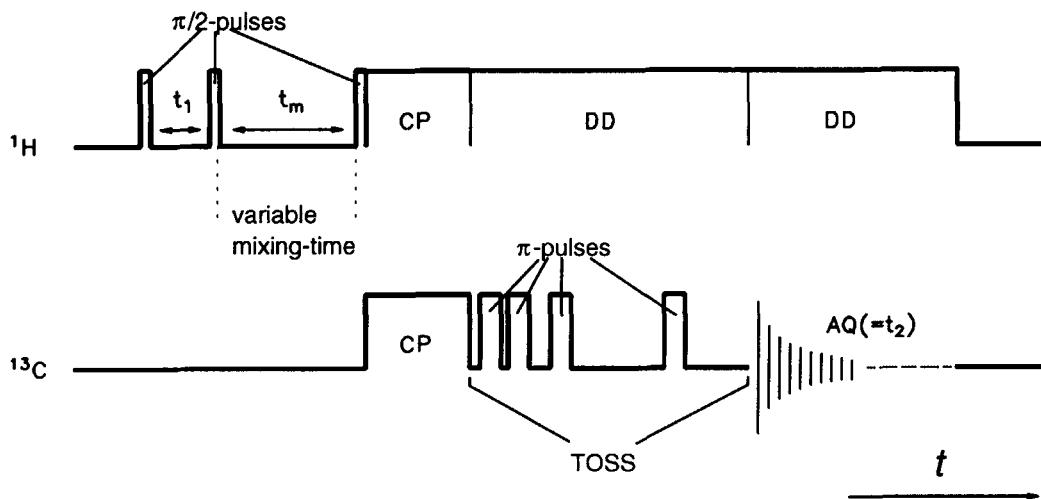


Figure 1 Schematic pulse scheme of the 2D-WISE experiment. Spin diffusion takes place during mixing time t_m .

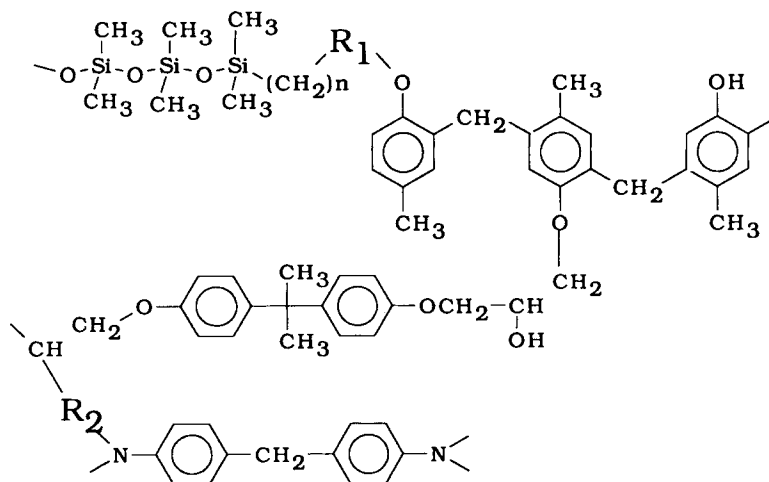


Figure 2 Generalized structure of modified epoxy molding materials.

1. a commercial cresol-novolak hardener,
2. the commercial compound Albiflex¹⁴ (a preadduct of a siloxane with an alkyl-phenol-novolak),
3. a modification compound SK, which was prepared by chemical coupling of an α,ω -epoxy siloxane component (siloxane chain length was about nine) with a cresol-novolak.

Figure 2 shows the generalized structure of the modified molding materials, the composition of the materials is summarized in Table I. The fillers used were commercial SiO_2 — fillers (Denka).

In all cases, the components were intensely mixed, preformed, and transfer molding processed at 100 bar and 175–190°C within 60–120 s. To reach a high filling factor for the NMR rotors, cylindrical samples of 1.8 mm diameter and 1.8 cm height were prepared using an appropriate molding. The high content of the filler in the investigated technical materials made, in general, long data acquisition times necessary. Additionally, two commercial materials, the standard molding material “Nitro HC 10” (Nitro) and the low-stress material “Aratronic 2180 VA”

(Ciba Geigy), were included in the investigations. The commercial material were also prepared with the same molding procedure.

RESULTS AND DISCUSSION

The prerequisite for an application of the above-mentioned more complex NMR techniques is the information about the chemical shifts of the different carbon atoms appearing in the chemical structure shown in Figure 2. Therefore, in Figure 3, the ¹³C-CP/MAS spectrum of a siloxane-modified epoxy novolak molding material recorded before curing and the corresponding difference spectrum (cured minus uncured) is displayed and a signal assignment is given. Due to the reaction of the epoxy groups with the novolak-OH groups, one observes a distinct decrease of the epoxy signals at 40–50 ppm and an increase of the ether signals at 70 ppm. The corresponding aryl-OH structure of the novolak is converted to an aryl-ether structure (156 ppm).

The effect of siloxane modification on the mo-

Table I Composition of Investigated Materials

	EPA ₀	EPA ₅	EPA ₁₀	SK	EPS ₀	EPS ₅
Epoxy component 1:	74.4%	67.6%	60.9%			
Epoxy component 2:					82.7%	75.7%
Albiflex-hardener:	—	12.5%	25%			
Siloxane-hardener:				100%	—	24.3%
Novolak-hardener:	25.6%	19.9%	14.1%		17.3%	—
Filler content	70%	70%	70%	70%	70%	70%
Siloxane-content: (calculated)	0%	5%	10%	20%	0%	5%

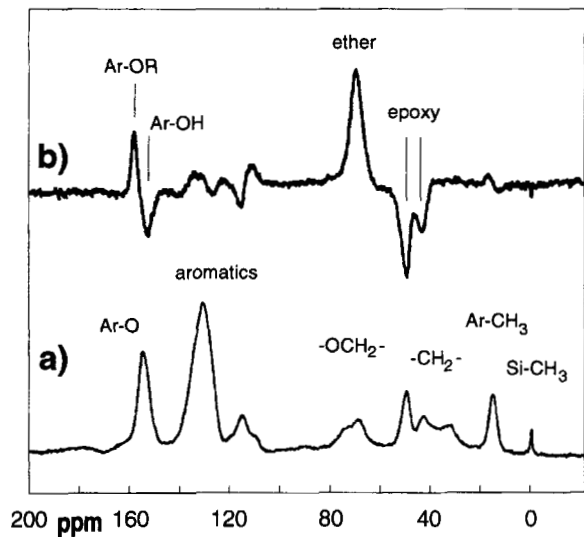


Figure 3 ^{13}C -CPMAS NMR spectrum of epoxy molding material and structural assignment. (a) before curing; (b) difference spectrum (cured minus uncured).

bility of the epoxy-novolak matrix is demonstrated by the results of a spin-lock experiment $T_{1\rho}(^{13}\text{C})$ for EPA₀ and EPA₁₀. Figure 4 shows the measured intensities of the ether groups (70 ppm) and the fits

from which the $T_{1\rho}(^{13}\text{C})$ relaxation times for short (0–6 ms) and long (6–42 ms) delay times are derived. The insert shows the results for short spin-lock times with an enlarged time scale. The calculated $T_{1\rho}(^{13}\text{C})$ relaxation times were 10 ms and 27 ms for EPA₀ and 11 ms and 28 ms for EPA₁₀ for short and long spin-lock times, respectively. The almost identical slopes indicate that there is no significant difference between siloxane-containing and siloxane-free material. The siloxane modification obviously leaves the mobility of the matrix in the mid-kHz region (50–60 kHz) almost unaffected.

It is remarkable that there are obviously two different relaxation mechanisms for the same structural element. The significant difference in the $T_{1\rho}(^{13}\text{C})$ relaxation times for short and long spin-lock times might be caused by areas of different motional behavior in the material. Vollenberg et al.^{15,16} could show, that in a filler-containing polymer system the polymer in the proximity of a filler particle is more rigid, so that the mobility is reduced compared to structural areas more apart of the filler particle. Thus, the short $T_{1\rho}(^{13}\text{C})$ relaxation times can be assigned to the more rigid parts of the material in the nearest neighborhood of a filler particle.

Temperature-dependent measurements of

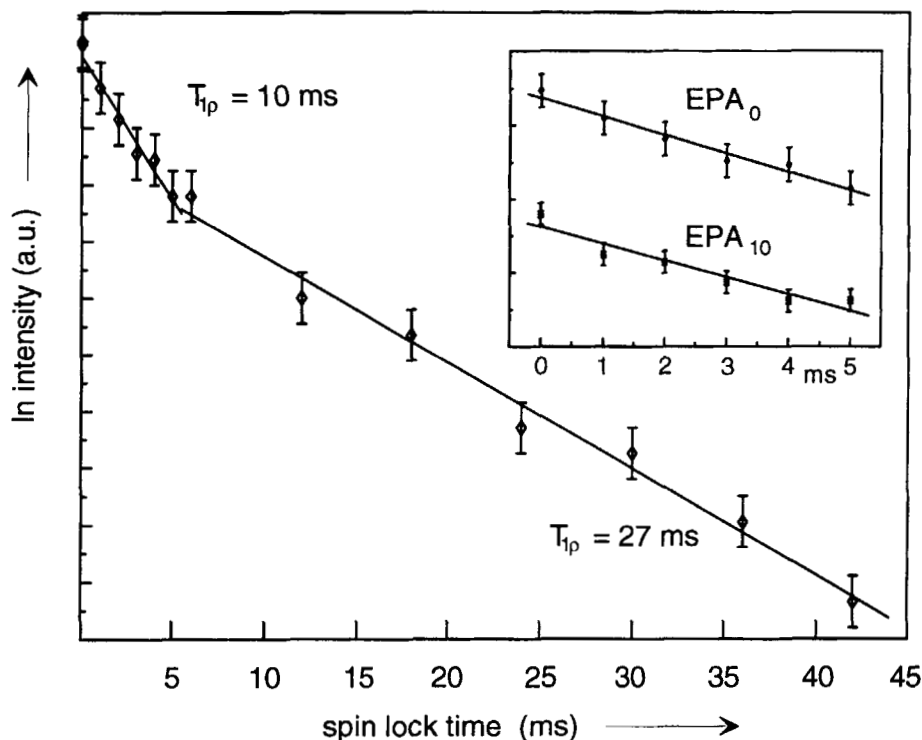


Figure 4 Spin-lock time dependence of the ether signal (70 ppm) of EPA₁₀ for the evaluation of $T_{1\rho}(^{13}\text{C})$ relaxation times. Insert shows the behaviour for short spin-lock times.

$T_{1\rho}(^{13}\text{C})$ relaxation can be correlated with mechanical relaxation determined by dynamic mechanical thermoanalysis (DMTA, see Fig. 5). With raising temperature, there is a strong decrease in the slope of the Si—CH₃ signal and a less pronounced decrease of the signal of aliphatic chains. Both observations are interpreted due to an increasing mobility of the corresponding structural elements. The activation of siloxane chain motion is assumed to start at temperatures about -120°C (the glass transition of pure polydimethyl-siloxane is known to be -123°C) and shows a strong temperature dependence, whereas the motion of aliphatic chains seems to start in the temperature range from 20° – 80°C . This indicates, that the β -relaxation in the DMTA loss modulus is caused by the onset of motions of aliphatic chains. Strong correlations could also be found between DMTA relaxations and slow motion sensitive NMR relaxations.

Figure 6 shows the variation of the slopes for the Si—CH₃—group and the matrices of different materials from which the $T_{1\rho}(^1\text{H})$ relaxation times compiled in Table II were evaluated. The term “matrix” stands for the signals of every structural element in the material except those of the Si—CH₃ groups. It can be noticed, that the $T_{1\rho}(^1\text{H})$ relaxation

time of $6\ \mu\text{s}$ is the same for all the polymeric backbone signals, regardless whether they belong to the standard material Nitto or to the low-stress material Aratronic. The different slopes proof a phase separation with the formation of siloxane domains for EPA₁₀ and Aratronic. The low siloxane content in EPA₅ and EPS₅ causes a larger error in the determination of the intensities, so that for EPA₅ a phase separation seems to be significant, whereas for EPS₅ this might not be true.

The differences in the $T_{1\rho}(^1\text{H})$ relaxation times between the Si—CH₃ groups in EPA₅ and EPA₁₀ indicate that there is no complete phase separation in these systems, i.e., parts of the siloxane remain homogeneously mixed with the epoxy-novolak matrix. If phase separation was complete, the relaxation times for the siloxane domains in both materials would be identical. The question, whether the longer $T_{1\rho}(^1\text{H})$ relaxation time for the siloxane phase in Aratronic might be caused by either a more complete phase separation or a different siloxane component could not be concluded.

The high mobility of the siloxane chains in the domains results in “sharp” signals in solid-state ^1H -NMR spectra compared to the broad signals from less mobile regions. If spin diffusion among the pro-

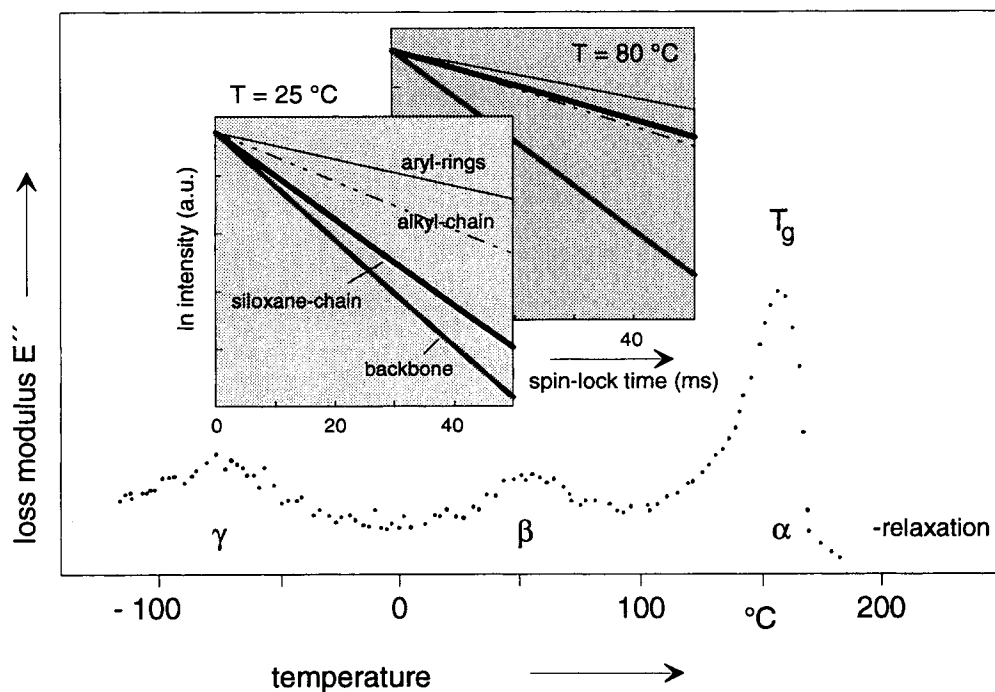


Figure 5 Loss modulus E'' from dynamic mechanical measurement of EPA₁₀ showing three different mechanical relaxations. Insert shows dependence of signal intensities from spin-lock time for the determination of $T_{1\rho}(^{13}\text{C})$ relaxation times at different temperatures in the region of the β -mechanical relaxation.

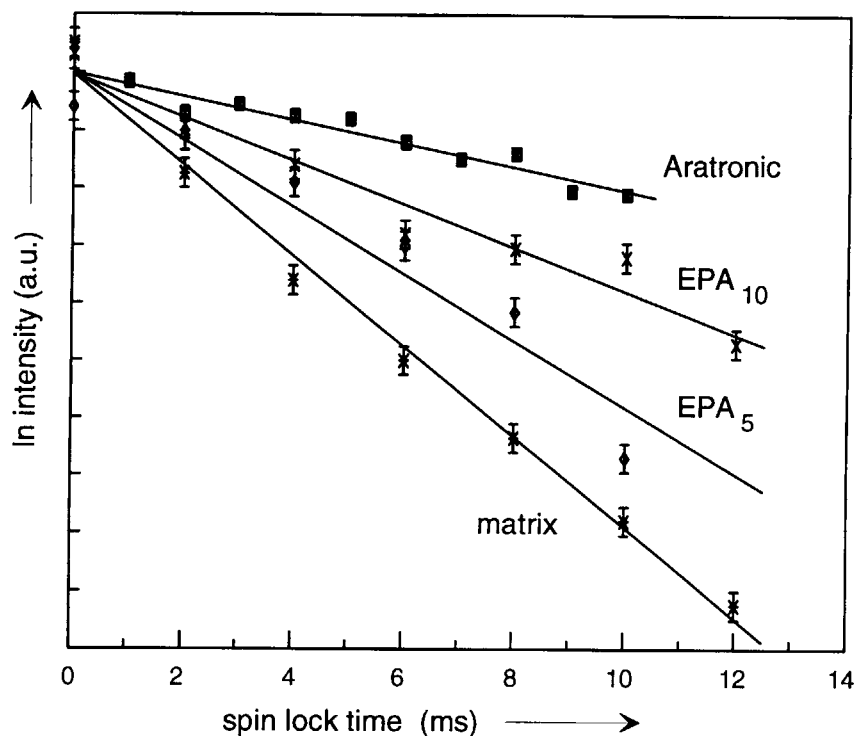


Figure 6 Spin-lock time dependence of signal intensity of the Si—CH₃ groups and the “matrices” in commercial and modified low-stress materials for the determination of $T_{1\rho}({}^1\text{H})$ relaxation times.

tons is effective, it leads to an equilibration, which results in a transfer of the “sharp” magnetization properties to neighboring structures. The kinetics of the magnetization transfer are mainly governed by the following material properties: the diameter of siloxane domains d_{so} , the size of the interphase between matrix and siloxane d_{if} , the distance between siloxane domains d_{de} , and the ${}^1\text{H}$ -spin diffusion constants in the siloxane domains D_{so} , in the interphase D_{if} , and in the matrix D_{de} . This has been detected by means of the 2D-WISE NMR experiment as changes in signal intensity (Fig. 7) for the model system SK: after a short mixing time (0.4 ms), there is only detectable magnetization for the Si—CH₃— signal at 1 ppm. After a mixing time of 1000 ms, this magnetization has been transferred to all other structures. Figure 8 shows exemplary this

raise of the intensity of the signal at 16 ppm, which originates from the methyl group of the cresolnovolak.

From the data in Figure 8 and a suitable chosen set of parameters (Table III), the size of siloxane domains d_{so} could be estimated by spin diffusion modeling;^{17,18} a domain size d_{so} of 4 nm was obtained for the siloxane domains in the SK system. Despite of its high filler content ($\geq 70\%$), this estimation was also possible for Aratronic. With a slightly different parameter set, a minimum domain size of 6 nm was obtained. For EPA₁₀, the WISE spectra did not show any magnetization transfer to structures outside the siloxane domains. This agrees with larger domain sizes in the μm range, which have also been detected by scanning electron microscopy, while spin diffusion only works on the nm scale.

Table II $T_{1\rho}({}^1\text{H})$ Relaxation Times of Siloxane Phase and Matrix in Molding Materials

	EPA ₀	EPA ₅	EPA ₁₀	EPS ₀	EPS ₅	Nitto	Aratronic
Matrix				6 ms ± 1 ms			
Si—CH ₃	—	8.5 ms	10 ms	—	7.3 ms	—	21 ms

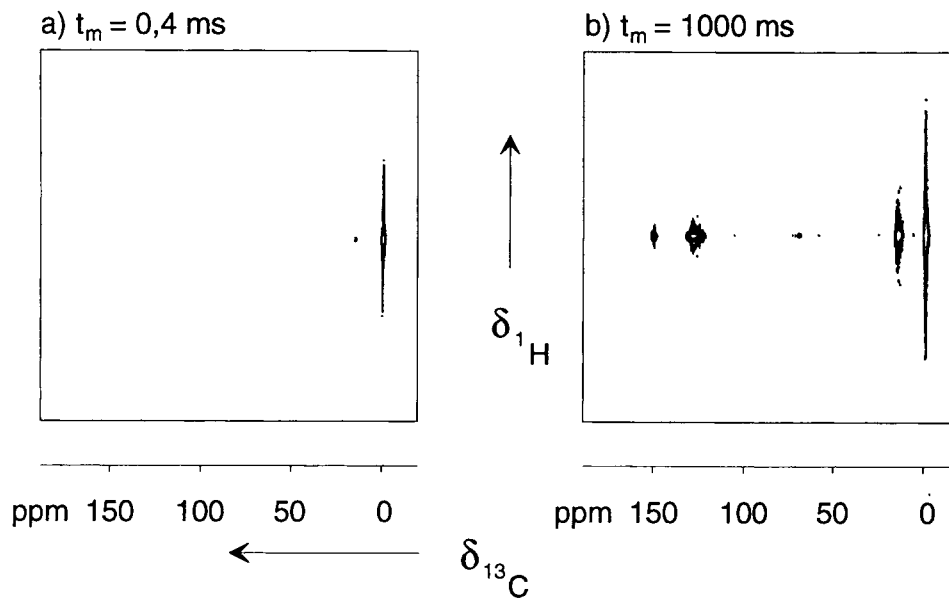


Figure 7 2D-WISE spectra of the SK sample recorded with short and long mixing times.

CONCLUSION

Based on standard epoxy-novolak materials, newly modified systems with low-stress characteristics could be synthesized using two different siloxane components. CPMAS solid-state NMR measurements are well suited for the characterization of

structure, molecular dynamics, and morphology in these systems, even in the case of highly filled, highly crosslinked molding materials.

By means of various relaxation time experiments, areas of different mobility and the effect of siloxane modification on the mobility of the duroplastic matrix could be investigated. $T_{1\rho}(^{13}\text{C})$ relaxation times

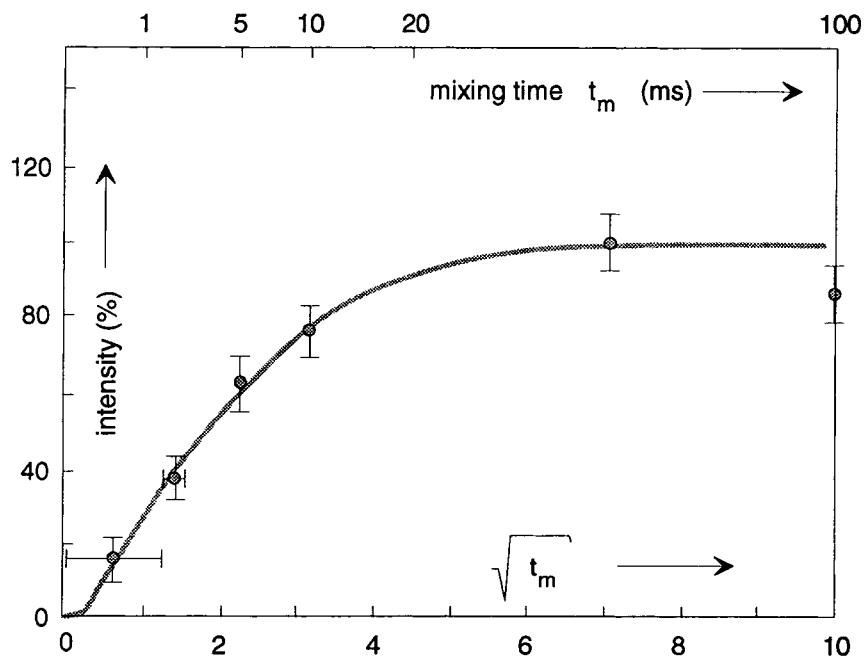


Figure 8 Intensity of the methyl signal (16 ppm) of the SK sample as a function of spin diffusion time (t_m) in the WISE-experiment and corresponding fit.

Table III Material Parameters for Spin-Diffusion Modeling

Parameter	SK system	Aratronic
d_{if}	0.4 nm	0.2 nm
d_{de}	2.6 nm	9.6 nm
D_{so}	0.06 nm ² /ms	0.02 nm ² /ms
D_{it}	0.28 nm ² /ms	0.26 nm ² /ms
D_{de}	0.50 nm ² /ms	0.50 nm ² /ms

could be used to detect the variation of mobility in the proximity of filler particles, whereas their temperature dependence allowed the identification of mechanical relaxations in filled low-stress duroplastics. Further results on the thermo analytical investigation of those modified materials are submitted in a second article.

For a morphological characterization $T_{1\rho}$ (¹H) relaxation allows a fast and unambiguous detection and assignment of phase separation. Materials, which are well-suited as low-stress duroplastics, show microphase separation with the formation of siloxane domains in the nm range coupled to the epoxy–novolak matrix. The new 2D-WISE NMR experiment even offers more detailed information about morphology. Using the spin-diffusion model it allows the estimation of domain sizes even in highly filled polymers.

The authors would like to thank S. Lehmann from the Max-Planck-Institut für Polymerforschung at Mainz for the spin-diffusion modeling calculations and M. Pyrlík from Hanse Chemie, Geesthacht for the Albiflex materials. Financial support from the “Fonds der chemischen Industrie” is gratefully acknowledged.

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Received December 29, 1993

Accepted April 27, 1994