

Effect of Ambient Atmosphere on Crosslinking of Polysilazanes

Ricardo Chavez,^{1,2} Emanuel Ionescu,¹ Corneliu Balan,³ Claudia Fasel,¹ Ralf Riedel¹

¹Technische Universität Darmstadt, Institut für Materialwissenschaft, Petersenstrasse 23, Darmstadt D-64287, Germany

²Robert Bosch GmbH, CR/APP4, Postfach 1131, Waiblingen 71301, Germany

³Hydraulics Department, Politechnica University Bucharest, Splaiul Independentei 313, Bucharest 060042, Romania

Received 9 March 2010; accepted 9 May 2010

DOI 10.1002/app.32777

Published online 27 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The influence of ambient atmosphere on the crosslinking process of two commercially available polysilazanes with different molecular units in the backbone structure (one polysilazane with and one without urea units) was studied at different temperatures using oscillatory rheometry under isothermal conditions. The measurements were performed using cone/plate, plate/plate, and Couette geometries to assess the influence of the contact surface of the samples with air on their crosslinking behavior. The crosslinking process of the investigated polysilazanes in ambient atmosphere was found to occur faster than that in inert atmosphere. DSC and FTIR-spectroscopic investigations indicate that hydrolysis and polycondensation processes occur in both polysilazanes when crosslinked in air.

Interestingly, the effect of moisture was found to be more pronounced in the case of the urea derivative. The evolution of the measured complex viscosity and dynamic moduli supported this finding. Furthermore, the variation of the time derivative of complex viscosity ($d\eta^*/dt$) emphasizes structural changes during crosslinking of the samples which were ascribed to their contact with the ambient atmosphere. This study emphasizes the high potential of rheometry in investigating the crosslinking behavior of polymers in inert and ambient atmosphere. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 794–802, 2011

Key words: polysilazanes; crosslinking; polymer rheology; viscoelastic properties

INTRODUCTION

Silicon-based polymers, such as polysiloxanes and polysilazanes, have been used in the last 3 decades as precursors for the synthesis of ceramics.¹ The overall process for the formation of polymer derived ceramics (PDCs) consists of three major steps: (1) synthesis of preceramic polymers from suitable monomers; (2) polymer crosslinking at moderated temperatures leading to an infusible organic/inorganic network (preceramic networks, duroplastics); (3) ceramization process (pyrolysis) of the crosslinked polymers, which are finally converted into inorganic amorphous materials by heat treatment at temperatures from 1000 to 1300°C.²

The crosslinking process is an important step in the PDC processing. Thus, during crosslinking the polymeric precursors are converted into organic/inorganic materials at low temperatures (100–400°C).

This transformation prevents the loss of low molecular weight components of the polymer precursors and fragmentation processes thereof during pyrolysis, and thus increases the ceramic yield. Furthermore, the crosslinking process leads to infusible polysilazanes (duroplastics) which retain their shape during pyrolysis as the ceramization process occurs without melting.

Crosslinking of polysilazanes can be achieved either thermally or using chemical reagents, such as catalysts or peroxides. There are four major reactions which can occur during the thermal crosslinking processes of appropriate substituted polysilazanes: transamination, dehydrocoupling (between Si–H and N–H resp. Si–H and Si–H groups), vinyl polymerization, and hydrosilylation.³

Hydrosilylation reaction occurs in oligosilazanes which contain Si–H and vinyl groups. It is a fast reaction even at lower temperatures (100–120°C) and leads to the formation of Si–C–Si and Si–C–C–Si bonds which are not affected by thermal depolymerisation reactions such as transamination or exchange of Si–N bonds. Thus, higher ceramic yield and higher carbon contents can be achieved in the final ceramic materials.⁴ Hydrosilylation can be also performed in the presence of catalysts, which remarkably increase the reaction rate.⁵ Dehydrogenation of

Correspondence to: E. Ionescu (ionescu@materials.tu-darmstadt.de).

Contract grant sponsor: Fonds der Chemischen Industrie.

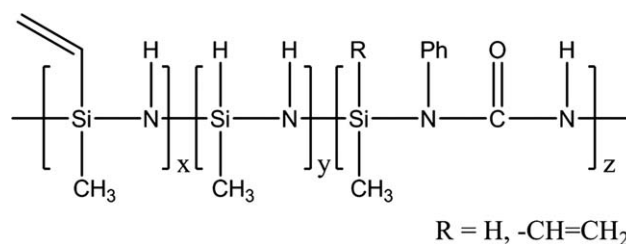
Si–H/N–H or Si–H/Si–H groups starts at higher temperatures (ca. 300°C) and lead to Si–N and Si–Si bond formation along with hydrogen evolution. Vinyl polymerization (polyaddition) reaction occurs at higher temperatures and involves no mass loss. Transamination reactions occur by thermal heating of oligosilazanes in a temperature range from about 200 to 400°C and are associated with a mass loss, i.e., amines, ammonia or oligomeric silazanes evolution, thus leading to a decrease in nitrogen content of the final ceramic materials. Furthermore, redistribution reactions at silicon atoms can occur, thus volatile silicon species, e.g., silanes, are formed and decrease the ceramic yield and the silicon content of the end ceramics.³

Whereas there are many rheological investigations published which are related to the visco-elastic properties^{6–10} and crosslinking behavior of polysiloxanes,^{11–15} only few studies concerning polysilazanes have been carried out. Especially, the influence of adding nanofillers such as multiwalled carbon nanotubes¹⁶ and functionalized single walled carbon nanotubes^{17,18} into polysilazanes has been analyzed. These studies were focused rather in understanding the interaction between the polymer and nanofiller, and the processability of the mixture before the crosslinking thereof. However, no systematic rheological investigations on the crosslinking behavior of polysilazanes have been reported yet. Therefore, there is still a lack of knowledge about the development of the rheological properties due to structural rearrangements of polysilazanes during crosslinking.

This article reports on a systematic study on the rheological properties as formed during crosslinking of polysilazanes in inert atmosphere and in air. The results emphasize that the crosslinking process of the polysilazanes is accelerated in air atmosphere. The development of the rheological properties of the investigated materials indicates a different crosslinking mechanism thereof if compared with the process performed in inert conditions. The results obtained from the differential scanning calorimetry (DSC) and FTIR-spectroscopic characterization show that hydrolysis and polycondensation processes occur when both polysilazanes are thermally treated under air atmosphere. Thus, crosslinking of polysilazanes in ambient conditions can be achieved at lower temperatures than in inert atmosphere. Furthermore, this study emphasizes the fact that rheometry is a powerful tool to investigate the crosslinking behavior of preceramic polymers.

EXPERIMENTAL

Two commercial polysilazanes (i.e., Ceraset PURS[®] and Ceraset HTT1800[®], Clariant GmbH, Sulzbach, Germany) were used as-received. The polysilazanes



Scheme 1 Chemical formula of Ceraset HTT1800 ($x = 0.2, y = 0.8, z = 0$) and Ceraset PURS ($x = 0.2, y = 0.75–0.79, z = 0.05–0.01$).

show the general chemical structure presented in Scheme 1.

Crosslinking was conducted by heating the polysilazanes under argon and in air, respectively. The rheological properties during this process were measured in strain-controlled oscillatory tests (i.e., constant strain amplitude - γ) using a MCR 301 rheometer from Physica Anton Paar, with two different geometries: (i) cone-plate (CP) with diameter 50 mm and cone angle of 1°, respectively (ii) plate-plate (PP) configuration, diameter 50 mm, and nominal gap of 0.4 mm. All the experiments have been performed at constant frequency $\omega = 1$ rad/s, with $\gamma = 1$ [-] for CP, respectively $\gamma = 0.01$ [-] for PP.

Time sweeps at constant frequency and amplitude were carried out under isothermal conditions at different temperatures. Continuous data acquisitions were performed for the cone-plate geometry and discrete measurements in time were recorded for the plate-plate configuration.

For the continuous measurements, the sample was kept in the gap between the cone and the plate during the whole periods of the experiments. It was observed in all the tests, where a curing reaction was detected, that only the material close to the rim has become solid at the end of the measurement; whilst the one at the center was clearly still a liquid. This behavior is an indication of the air influence on the thermal crosslinking of the samples, as the material at the rim was in direct contact with the air. Therefore, beyond a certain threshold of temperature, it might be expected that the material in direct contact with air will be crosslinked in shorter times, in comparison to the samples thermally treated in an inert atmosphere.

For the case of the discrete experiments, the upper plate was kept at the measuring position only during the time of one measured point, not during the whole time sweep as in the CP case. Using this method, the sample (heated at constant temperature) was in direct contact with the air during almost the whole test period. In contrast to the CP continuous measurements, at the end of time sweeps the sample was completely crosslinked.

TABLE I
Temperature Program Used for the DSC Analyses

Step	Initial temperature (°C)	End temperature (°C)	Temperature rate (°C/min)
First heating	-50	250	10
First cooling	250	0	10
Second heating	0	250	10
Second cooling	250	30	10

Time sweeps at constant frequency and shear stress amplitude were carried out under isothermal conditions at different temperatures using Couette geometry (concentric cylinders). The rheological properties of both polysilazanes were measured using the Couette geometry in stress-controlled test in a SR200 rheometer (Rheometrics). The employed Couette system was sealed with silicone oil using the procedure described by Balan and Riedel.¹⁹ The samples were placed in the Couette's cup and subsequently, the inner cylinder was put at the measuring position. Silicone oil was used to seal the sample's surface in contact with air to avoid air contact during the time sweeps.

DSC analyses were performed with a DSC 200 F3 Maia[®] device (Netzsch Gerätebau GmbH, Selb, Germany). The measurements were carried out under N₂ and O₂ atmospheres according to the temperature program shown in Table I.

The IR-spectroscopic characterization was performed with a 670-IR FT-IR spectrometer from Varian, using an ATR unit to study the region of wave numbers between 4000 and 700 cm⁻¹.

RESULTS AND DISCUSSION

As mentioned above, the thermal crosslinking of Ceraset PURS was studied using CP and PP geometries. First, the characterization of the samples exposed to air at the rim (CP geometry) was carried out at four different temperatures, i.e., 80, 100, 120, and 140°C (Fig. 1 bottom). At 80°C, no appreciable changes of the complex viscosity occurred. By using higher temperatures, a curing reaction can be analyzed and consequently the measured torque (i.e., the complex viscosity) increases fast. Furthermore, it can be seen in Figure 2 that by increasing the temperature, the samples are cured faster.

Figure 1 shows also the results obtained for samples whose complete surface was in contact with air during the heating (Fig. 1 top). The final measured viscosities obtained for the samples with air contact only at the rim (CP geometry) were found to be lower than those where the whole sample surface was in contact with air (PP geometry), especially at 140°C. At this temperature, the final viscosity meas-

ured with the PP geometry was two orders of magnitude higher than that of the sample measured in CP geometry. Obviously, the determined viscosities do not represent an intrinsic quantitative value of the sample viscosities at that temperatures (as the tests took place under the influence of air), but the measurements have a real qualitative value for the investigations of the crosslinking process.

To get more information about the thermal crosslinking process, the measured complex viscosity derivative with respect to the time, $d\eta^*/dt$, was calculated for the cured samples. This parameter can provide information about the development of the crosslinking process and changes that took place within the structure of the investigated materials at different times. The results obtained for the samples that suffered from air contact only at the rim and those for the samples whose whole surface was in contact with air are shown in Figure 2.

It can be taken from Figure 2 (bottom) that in the case of an isothermal treatment at 100, 120, and 140°C a maximum in the complex viscosity

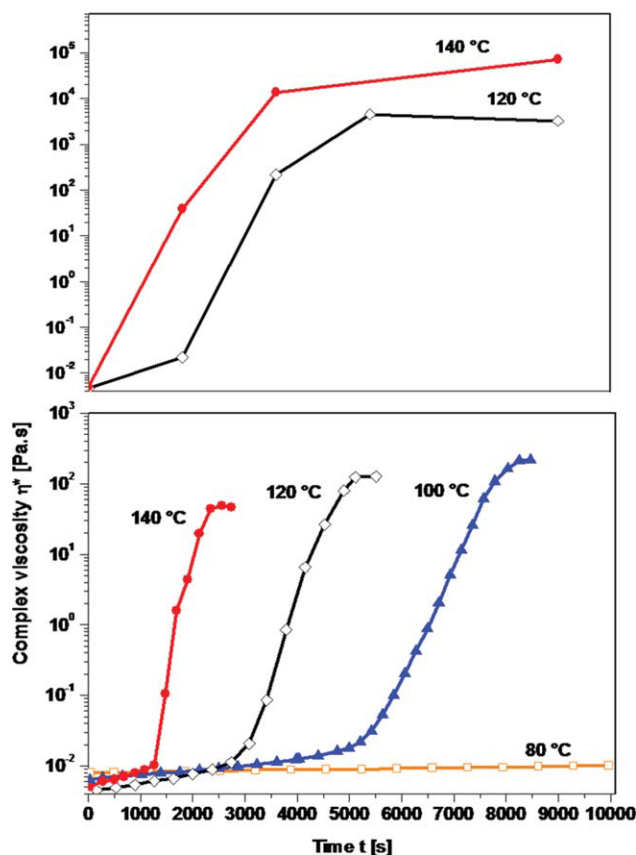


Figure 1 Evolution of the complex viscosity of Ceraset PURS samples during isothermal crosslinking at different temperatures: samples exposed only at the rim to air (CP geometry)—bottom; samples whose complete surface was in contact with air (PP geometry)—top. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

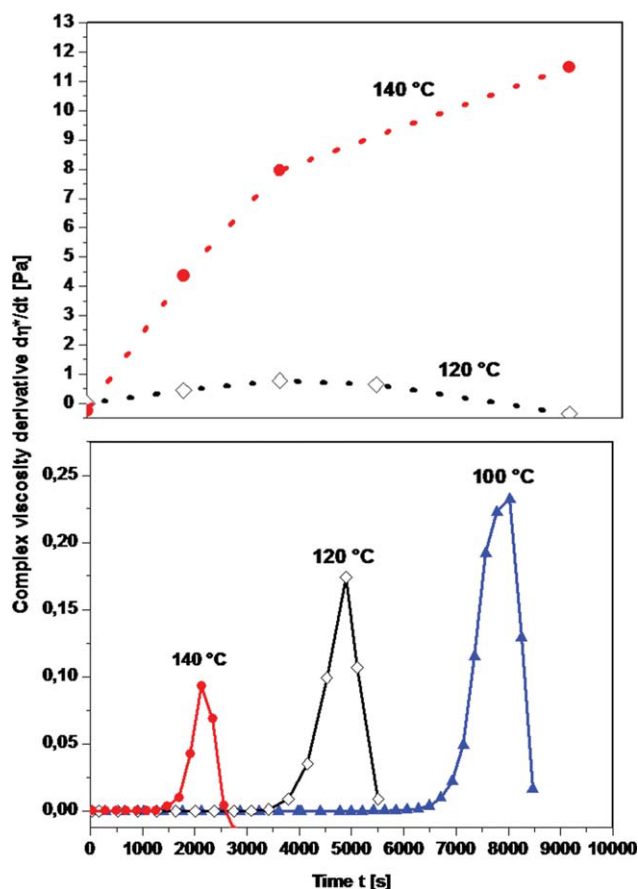


Figure 2 Evolution the first derivative of the complex viscosity for the Cereset PURS samples: samples exposed to air only at rim (CP geometry)—bottom; and samples with complete surface exposition to air (PP geometry)—top. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

derivative is obtained, which occurs in shorter times with increasing temperature. Furthermore, the amount of complex viscosity derivative at the maximum decreases with increasing temperature. This behavior might be a consequence of diffusion processes and another indication of a possible influence of air on the crosslinking process. By carrying out crosslinking at higher temperatures, there is more energy available for the reaction, and therefore, it proceeds faster. However, as the crosslinking process advances, the viscosity strongly increases and thus air diffusion is hindered. As the curing reaction occurs faster at higher temperatures, the air diffusion starts to become slower. Thus, the crosslinking process starts earlier at higher temperatures but cannot develop with rates as high as for lower temperatures.

However, comparing the evolution of the complex viscosity derivatives in Figure 2 (bottom and top), different tendencies can be discussed. First, the values of the derivatives obtained for the samples where the whole surface was in contact with air (PP geometry) are higher than those obtained for the

samples with air contact only at the rim (CP geometry). These results are in line with those found for the complex viscosity. Since in the PP measurements the whole sample surface was exposed to air, the air can diffuse via a higher number of possible paths. This situation could lead to higher crosslinking rates and a more homogeneously developed reaction within these samples, phenomena which are evident at 140 °C.

Moreover, it can be seen in Figure 2 (top) that the sample crosslinked at 140 °C does not present a decrease in the viscosity derivative within 10,000s. This result might be a consequence of the higher amount of energy required for the reaction or of the less hindered air diffusion at this temperature.

The gel point of a crosslinking polymer is defined by the time at which the storage (G') and loss (G'') moduli have the same value, the so-called “cross point;” i.e., the transition from liquid behavior to gel-like (solid) behavior.²⁰ In Figure 3 (bottom and

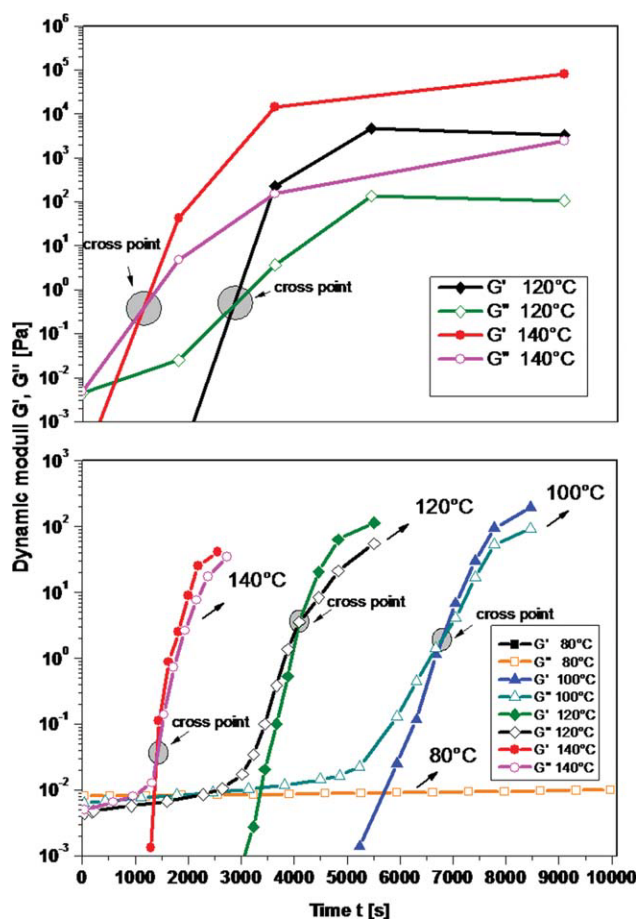


Figure 3 Evolution of the dynamic moduli (G' , G'') of the Cereset PURS samples during their isothermal crosslinking at different temperatures: samples exposed to air only at rim (CP geometry)—bottom; and samples with complete surface exposed to air (PP geometry)—top. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Gel Points Measured for Ceraset PURS (CP and PP
Geometry, respectively)

Temperature (°C)	Gel point (CP geometry) (s)	Gel point (PP geometry) (s)
100	~ 6500	NA
120	~ 4000	~ 3000
140	~ 1500	~ 1000

top), the evolution of G' and G'' in time is depicted for the samples exposed to air only at the rim (CP geometry) and for the samples which complete surface was in contact with air (PP geometry), respectively. By comparing the evolution of dynamic moduli in Figure 3 (bottom and top), one can conclude that by increasing the temperature, shorter times to achieve the gel point are observed for all the samples. However, the samples with the whole surface in direct contact with air (PP geometry) exhibit shorter times to reach the gel point than the samples with air contact only at the rim (CP geometry)

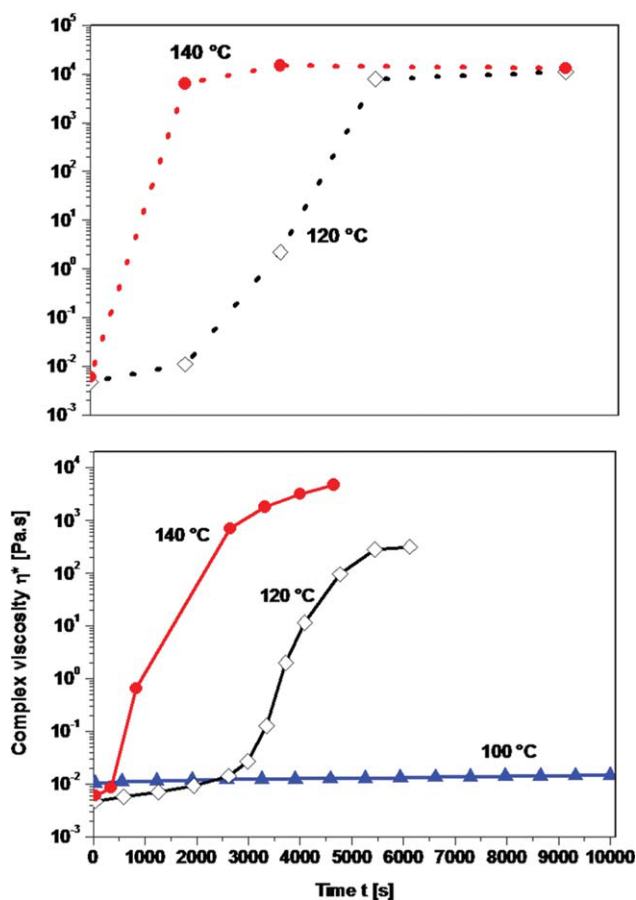


Figure 4 Evolution of the complex viscosity during the isothermal crosslinking of Ceraset HTT1800 at different temperatures: CP geometry (bottom) and PP geometry (top). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Table II). These results are in agreement with the trends analyzed for the isothermal development of the measured complex viscosity derivatives.

The polysilazane Ceraset HTT1800 was also studied by the same methodology. Some samples were exposed to air only at the rim (CP geometry), whereas others suffered from air contact on the complete surface (PP geometry) (Fig. 4). One can observe that this material shows a similar behavior as that of the Ceraset PURS. By using higher temperatures, the viscosity maximum is reached in shorter times. Furthermore, the measured viscosities obtained for the materials with the whole surface in contact with the air (PP geometry) presented slightly higher values than those with contact only at the rim. However, the main difference between the tested samples is that Ceraset PURS starts to crosslink at temperatures as low as 100°C, whereas Ceraset HTT1800 shows this behavior at temperatures exceeding 120°C.

As in the case of Ceraset PURS, the complex viscosity derivative with respect to the time was

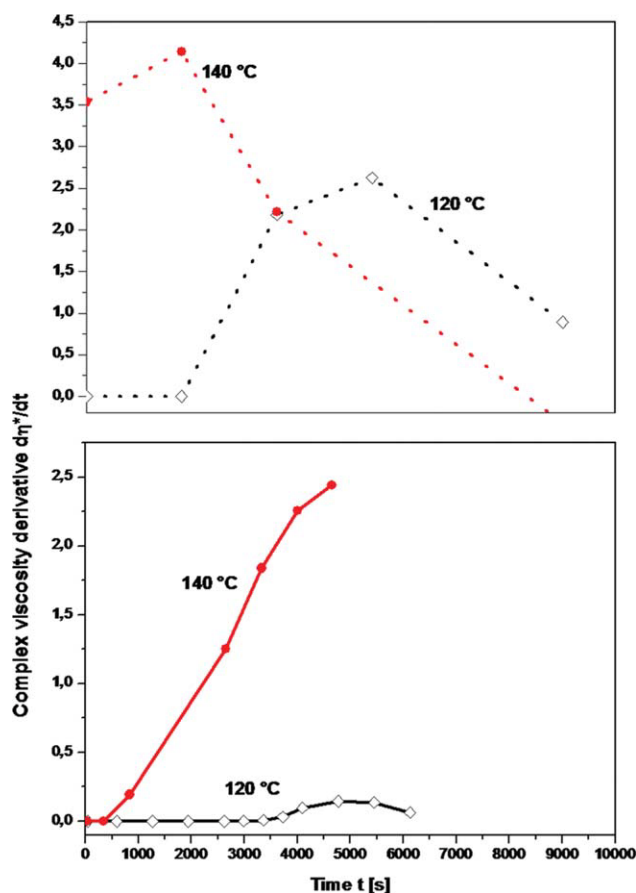


Figure 5 Evolution of the first derivative of the complex viscosity during isothermal crosslinking of Ceraset HTT1800 at different temperatures: samples exposed to air only at the rim (CP geometry)—bottom; samples with complete surface exposed to air (PP geometry)—top. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Gel Points Measured for Ceraset HTT1800 by Using CP and PP Geometries

Temperature (°C)	Gel point (CP geometry) (s)	Gel point (PP geometry) (s)
120	~ 3500	~ 3900
140	~ 1200	~ 700

calculated in order to get more information about the crosslinking process. The obtained results for the samples in contact with air and with CP geometry and for the samples with PP geometry are shown in Figure 5 (bottom and top, respectively). It is clearly seen that the derivatives of the complex viscosity for the Ceraset HTT1800 samples in contact with air at the rim present a different behavior than those of Ceraset PURS samples. Thus, only the HTT1800 sample crosslinked at 120°C present the form of a peak (increase and decrease of the derivative's

value) within the measured time, whereas the sample cured at 140°C present a maximum with no further decrease. These results indicate that Ceraset HTT1800 measured at 140°C is still undergoing a crosslinking process, whereas the sample measured at 120°C is not further reacting. This behavior might be related to the differences in the air diffusion at these temperatures. It seems that air can continue to diffuse within the sample at 140°C and thus probably indicates a thermally activated crosslinking occurring.

By comparing the results obtained for Ceraset HTT1800 measured with CP and PP geometry, one can conclude that at 120°C the maximum of the complex viscosity derivative is achieved at similar times (3500 and 3900 s, respectively). This result indicates that the crosslinking occurs almost at the same rate in both samples. However, the derivative maximum for the sample measured with PP geometry presents a higher value than that of the sample measured with CP geometry, indicating that crosslinking is taking place more homogeneously within

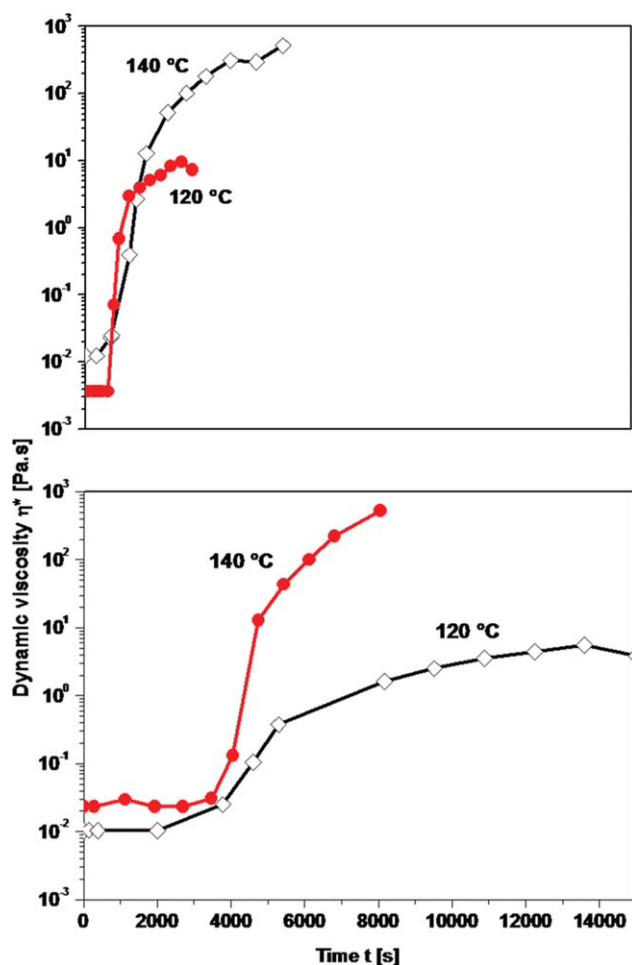


Figure 6 Evolution of the complex viscosity of Ceraset PURS (bottom) and HTT1800 (top) isothermally cured at 120 and 140°C, using Couette geometry ($\omega = 1$ rad/s; shear stress amplitude $\tau = 10$ Pa, nonsealed samples). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

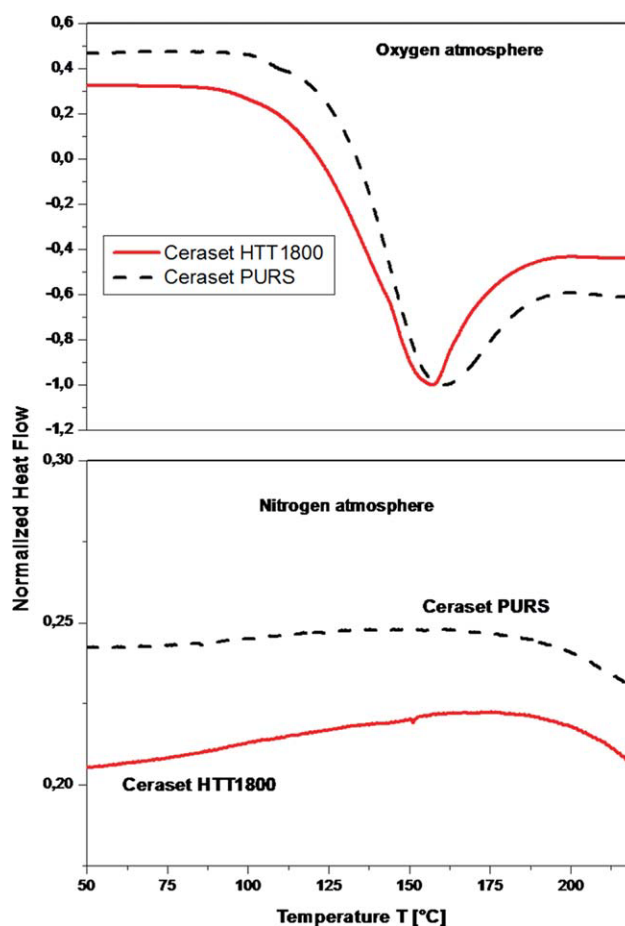


Figure 7 DSC analysis of Ceraset PURS and Ceraset HTT1800: under nitrogen atmosphere (bottom) and under dry oxygen atmosphere (top). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

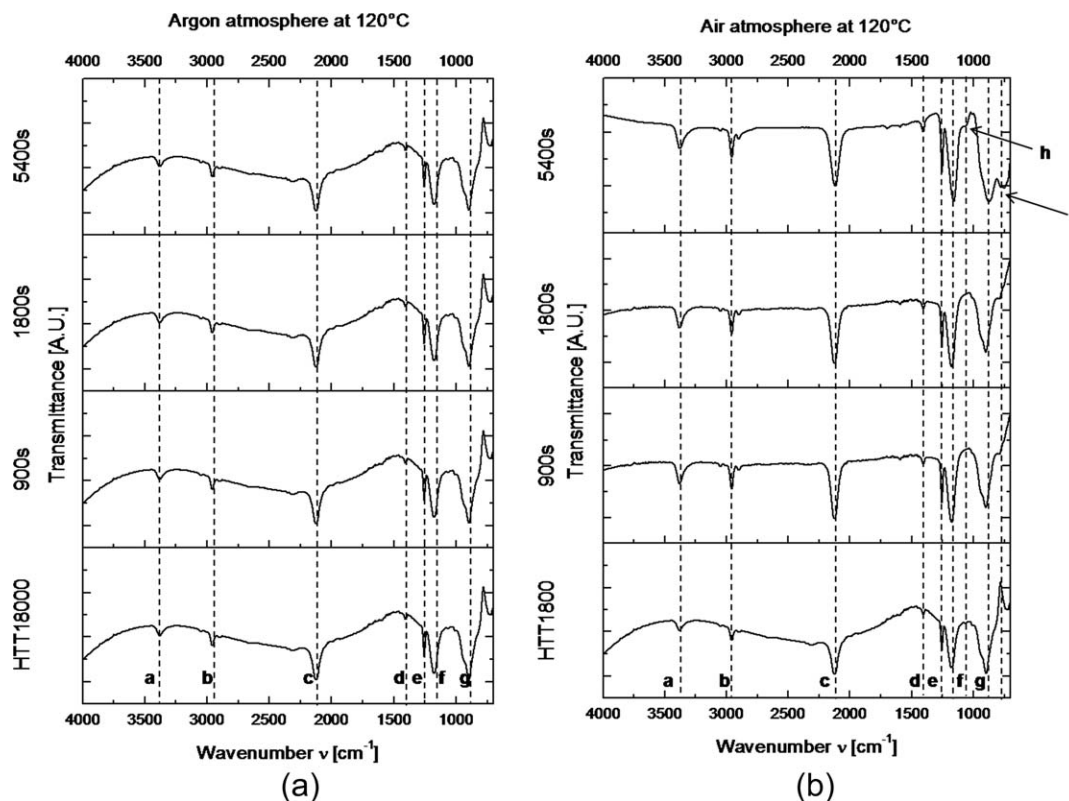


Figure 8 FTIR-spectra obtained for Ceraset HTT1800 samples upon heating at 120°C under argon (a) and air atmosphere (b): (a, N–H; b, C–H; c, Si–H; d, C–H; e, Si–CH₃; f, Si₂N–H; g, Si–CH₃; h and i, Si–O–Si).

the PP sample. This behavior is similar to that of Ceraset PURS. However, the air contact of the sample surface seems to have an enhanced influence on the crosslinking process of Ceraset PURS than that of Ceraset HTT1800.

Furthermore, Ceraset HTT1800 crosslinked at 140°C exhibited more pronounced differences in their complex viscosity derivative than those cured at 120°C. This finding can be explained by higher air diffusion into the polymer at higher temperatures which leads to a faster crosslinking process.

The gel points obtained from the evolution of G' and G'' moduli during the cross-linking process at different temperatures for the HTT1800-based samples measured with CP and PP geometry are summarized in Table III. They do not differ so much in the procedures for Ceraset HTT1800, as it is the case for Ceraset PURS. This behavior clearly indicates that the air atmosphere has a stronger influence on the cross-linking process of Ceraset PURS than on that of Ceraset HTT1800.

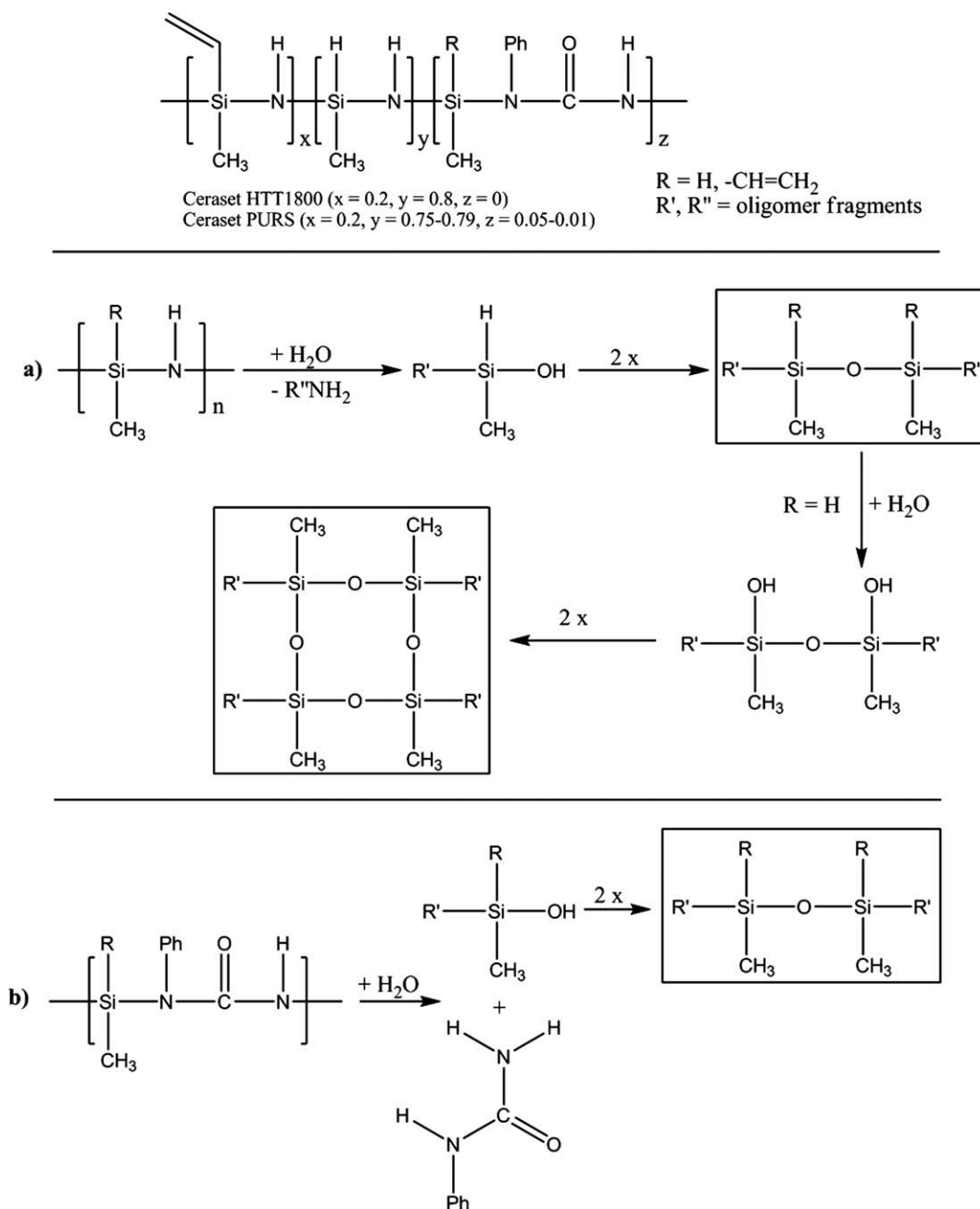
By comparing the evolution of the complex viscosity of Ceraset PURS and Ceraset HTT1800 during crosslinking at 120°C, one can conclude that Ceraset PURS exhibits higher viscosity values up to 5000 s; however, both polysilazanes reach similar viscosity values after 10,000 s of isothermal curing. Upon increasing the crosslinking temperature to 140°C,

Ceraset HTT1800 presents higher viscosity values than that of Ceraset PURS, supporting the faster curing process in the case of HTT1800.

The isothermal evolution of the complex viscosity of the polysilazane samples was investigated also by using the Couette geometry. The Ceraset PURS samples which were not sealed (and thus had contact with ambient atmosphere) showed an increase of their complex viscosity in time (Fig. 6 bottom), whereas the viscosity of the sealed samples remained constant. The same behavior has been observed also for Ceraset HTT1800 (Fig. 6 top). However, one should note that crosslinking of HTT1800 starts at 1800 s (Fig. 6 top), whereas that of PURS starts at 3800 s (Fig. 6 bottom).

The present finding points out that the higher complex viscosity observed for Ceraset HTT1800 at 140°C with respect to Ceraset PURS has to be discussed as a consequence of higher reactivity of HTT1800 towards air exposure and not in terms of a thermally activated crosslinking reaction.

The rheological investigations performed on the crosslinking behavior of the polysilazane samples in argon and air atmosphere indicate that in inert atmosphere, temperatures beyond 140°C are needed in order to activate crosslinking, whereas in air curing occurs at temperatures as low as 120°C. Furthermore, the results emphasize that the crosslinking



Scheme 2 Hydrolysis and polycondensation reactions which occur in the polysilazane-based samples upon heating in air atmosphere. Whereas in HTT1800 only reaction (a) can occur, Ceraset PURS can also react as presented in (b).

process of polysilazanes in air is related to the molecular structure directed reactivity of the polysilazane and cannot be considered as a thermally activated process at the investigated temperatures.

To attain information on the curing process of polysilazanes in air atmosphere, DSC analysis and FTIR spectroscopic investigations were performed with both polymers. DSC measurements were conducted under nitrogen and dry oxygen atmosphere, respectively, at temperatures from r.t. to 250°C (Fig. 7).

Under inert atmosphere, no exothermic process (i.e., crosslinking reaction) was detected for both

polysilazanes in the investigated temperature range (Fig. 7 bottom). This is in good agreement with the evolution of the rheological properties of both materials during isothermal crosslinking in inert atmosphere. During thermal treatment in dry oxygen atmosphere, an exothermic process was identified for both polysilazanes (Fig. 7 top). However, the onset temperatures of this process were found to be higher than 120–130°C. Thus, one can conclude that dry oxygen is not responsible for the changes in the rheological properties of Ceraset PURS and Ceraset HTT1800 at the studied temperatures (120°C and

140°C). As oxygen does not affect the crosslinking behavior of both polysilazanes at temperatures up to 140°C, it is the moisture which induces the curing of the polysilazanes at temperatures below 140°C. To elucidate the effect of moisture on the crosslinking behavior of both polysilazanes, *ex situ* FTIR spectroscopic measurements were performed on samples cured at temperatures of 120 and 140°C in inert and air atmosphere. The FTIR spectra obtained for Ceraset HTT1800 heated under argon and air atmosphere at 120°C are presented in Figure 8.

Whereas the samples thermally treated under inert atmosphere do not show any change with respect to pure HTT1800 (even after heating at 140°C), two new absorption bands at 1067 and 764 cm^{-1} appear upon heating in air at 120 and 140°C (**h** and **i**, in Fig. 8), which correspond to the presence of Si—O bonds. The same behavior was found also in the case of Ceraset PURS heated in ambient atmosphere. The IR spectra of the heat treated samples of both polysilazanes indicate that hydrolysis and polycondensation reactions occur. Thus, water reacts with the silicon-nitrogen bond to produce silanol groups which undergo condensation and lead to siloxane units and consequently to an increase in the crosslinking grade of the polysilazanes (Scheme 2). However, HTT1800 undergoes only the reaction pathway (a), whereas Ceraset PURS additionally can react as described in (b) (Scheme 2). The rheology investigations indicate that the hydrolytic elimination of 1-phenyl urea probably occurs at lower temperatures than the cleavage of Si—N bonds in the case of hydrogen or vinyl substitution at silicon.

CONCLUSIONS

This study reports on the influence of ambient atmosphere on the crosslinking behavior of polysilazanes which was analyzed via rheological investigations. Additional DSC and FTIR spectroscopic measurements showed that the polysilazanes undergo partial hydrolysis upon heating in ambient atmosphere, thus the Si—N bonds react with moisture leading to silanol groups which further polycondensate to siloxane units. In contrast, heating of the polysilazanes in inert atmosphere revealed that no crosslinking occurs up to 140°C. This finding also excludes the possibility of thermally activated crosslinking reactions in the studied temperature range.

Furthermore, the effect of moisture on the crosslinking process was found to depend on the polysilazane structure. Thus, moisture-induced crosslinking is more pronounced for Ceraset PURS than for

Ceraset HTT1800. By being in contact with air, Ceraset PURS cures at lower temperatures (100°C) and presents larger differences in the time derivatives of the complex viscosity by changing the measurement geometry (CP vs. PP). According to the information provided by the supplier, the only difference between Ceraset PURS and Ceraset HTT1800 is the small amount of urea groups present in the Ceraset PURS molecular structure. Consequently, the observed differences in the crosslinking behavior of both materials are due to the presence of urea units enhancing the reactivity of Ceraset PURS toward hydrolysis in ambient atmosphere.

The rheological investigations on the MC 301 Paar-Physica rheometer were performed at the Laboratory "Matter-Field Interactions" in the Bioengineering and Biotechnology Department of Politechnica University Bucharest.

References

- Riedel, R.; Mera, G.; Hauser, R.; Kloneczynski, A. *J Cer Soc Jpn* 2006, 114, 425.
- Ionescu, E.; Babonneau, F.; Gervais, C. In: *Polymer Derived Ceramics*; Colombo, P.; Riedel, R.; Soraru, G. D.; Kleebe, H.-J., Eds.; DEStech Publications, Inc.: Lancaster, PA, USA, 2009; p 108.
- Kroke, E.; Li, Y.; Konetschny, C.; Lecomte, E.; Fasel, C.; Riedel, R. *Mater Sci Eng R* 2000, 26, 97.
- Choong Kwet Yive, N. S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem Mater* 1992, 4, 141.
- Lavedrine, A.; Bahloul, D.; Goursat, P.; Choong Kwet Yive, N. S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J Eur Cer Soc* 1991, 8, 221.
- Ishida, H.; Shick, R.; Hurwitz, F. *Macromolecules* 1990, 23, 5279.
- Martinez, J. E.; Combe, E. C.; Pesun, I. *J Dental Mater* 2001, 17, 471.
- Swallow, F. E. *J Appl Polym Sci* 2001, 84, 2533.
- Beigbeder, A.; Bruzard, S.; Médéric, P.; Aubry, T.; Grohens, Y. *Polymer* 2005, 46, 12279.
- Balan, C.; Riedel, R. *J Optoe Adv Mater* 2006, 8, 648.
- Katz, D.; Zewi, I. G. *J Polym Sci* 1974, 46, 139.
- Walter, S.; Suttor, D.; Emy, T.; Hahn, B.; Greil, P. *J Eur Ceram Soc* 1996, 16, 387.
- Tixier, T.; Tordjeman, P. *Polymer* 2003, 44, 6937.
- Harshe, R.; Balan, C.; Riedel, R. *J Eur Ceram Soc* 2004, 24, 3471.
- Ngoumeni-Yappi, R.; Fasel, C.; Riedel, R.; Ischenko, V.; Pippel, E.; Woltersdorf, J.; Clade, J. *Chem Mater* 2008, 20, 3601.
- Kokott, S.; Heymann, L.; Motz, G. *J Eur Ceram Soc* 2008, 28, 1015.
- Li, Y.; Fernandez-Recio, L.; Gerstel, P.; Srot, V.; Van Aken, P.; Kaiser, G.; Burghard, M. *J Chem Mater* 2008, 20, 5593.
- Katsuda, Y.; Gerstel, P.; Narayanan, J.; Bill, J.; Aldinger, F. *J Eur Ceram Soc* 2006, 26, 3399.
- Balan, C.; Riedel, R. *Appl Rheol* 2003, 13, 251.
- Winter, H. H. *Polym Eng Sci* 1987, 27, 22.