

MONITORING OF CURING PROCESS OF SILOXANE RESIN BY DIELECTRIC ANALYSIS

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ABSTRACT

The knowledge of the curing process of polysiloxane resin is an important factor for the optimal preparation of the precursor of ceramic materials/composites/. It was observed that different physical method explaining the cure process e.g. /IR, NMR/ and examined experimentally the method of dielectric analyses/DA/. It was found that the method DA with the addition of the dopant makes the monitored system to increase its conductivity for the certain type of polymer. This enables to influence the properties of the final composite during its curing with the help of the appropriately selected temperature and pressure depending on time.

KEYWORDS: polysiloxane resins; dielectric analyse; curing process; dopant

INTRODUCTION

Siloxane (silicone) resins rank among a group of polyorganosiloxanes in where the silicone atom is bonded with another one by oxygen as bridging atom. The remained bonds of silicone are usually occupied by hydrocarbon substituents. The ratio of organic substituents to silicone atoms (-R/Si-) is less than 2, so it leads to indicate presence of branched chains in polymers (Mleziva and Šňupárek, 2000). The silicone resins originate from a blend of mono-, di- and trifunctional monomers in most case from methyl- and phenylchlorosilanes. The reaction path runs through stages of partial condensation of siloxanes, containing 3-6 % silanol group (Smith, 1991).

Observation from DSC measurements shows that the silicone resins are typical amorphous polymers with glass transition temperature $T_g = 40 - 46$ °C (Takahashi et al., 2001).

The siloxane resins may exist as solution, emulsion and in solid form.

The final product of resin transformation after curing is insoluble and infusible. The structure is shown at Figure 1 (Reuther, 1981).

This structure is netting (after full evaporation of solvent) at temperature 200-240 °C for 1-5 hours (Mleziva and Šňupárek, 2001). The molar mass increases within curing process owing to the condensation of the presence of hydroxyl- or alkoxy-groups (Takahashi et al., 2001) to reach the full network in the end (Noll, 1968). The cured resin

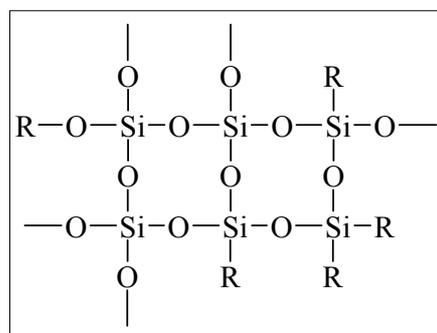


Fig. 1 Structure of cured siloxane resin

contains even 0.5-1.5% wt. silanol groups (Smith, 1991). The properties of the cured siloxane resins are not influenced by the presence of low concentration of the remained non-reacted hydroxyl groups. The network formation proceeds very promptly at the beginning, then formation rate falls gradually until the final steric structure of polymer network is created.

It is possible to reduce curing time or temperature by using some of many available catalysators (Smith, 1991). Metallic complex compounds (Co, Pb, Zn) with acceptable amines (Krauss and Kubens, 1956) are most used. Their application also leads the cured system to higher heat and storage stability. Possible another way to cure the siloxane resins is by ultraviolet radiation (USP 2003008081 A1 9 Jan, 2003).

The silicon resins are applied to production of paints and coatings, as composite matrix for laminate boards and moulding compounds and in impregnated form in fibre, leather and woven reinforced composites as well. Very interesting is the application of the polysiloxanes as the precursors for preparation or direct production of ceramic materials (Blackglass). Blackglass is a pyrolyzed thermally stable carbon, glass or ceramic fibre composite with polysiloxane matrix. (Smith, 1991) and is prospect material for the application in hot and oxidative environment.

Owing to last mentioned example, Blackglass, it is very important to pursue continuously the development of curing on line, then to find an optimal time to apply press to the moulding blend.

The investigation to modify of the cure process in situ is very important for the understanding and optimization (Chemistry, 1981). It is essential to determine the right time to press to get the mould piece with required property, for example content of reinforcement or reduced content of voids etc.

At this time the cure process is pursued by various methods, such as infrared spectroscopy (Takahashi et al., 2001; Kakudo et al., 1953; McDonald, 1957; Brus and Dybal, 2002), or nuclear magnetic resonance (Newmark and Copley, 1984; Chem.Abstr., 1984). But these methods do not describe the real-time cure process. Dielectric analysis is further possible method for monitoring the cure process of thermosetting resins (Chemistry, 1981; Wang et al., 2003; Pichaud et al., 1999; Corezzi et al., 1999; Krevelen, 1990). During curing, ageing or synthesis, there are some changes in electrical field, thus they influence movements of their ions and dipoles, which can be scanned at time (Wang et al., 2003).

Large number of studies about DA concerns the results of the research of the cure process of epoxide and polyimide resin system, including modification with polysiloxanes. So the question is if the last mentioned realised application in this system is transferable to the application in the polysiloxane system.

The purpose of the present study is to certify the possibility of application DA monitoring thermal cure of thermosetting polysiloxane resin, and to try to interpret just acquired results in the siloxane system.

EXPERIMENTAL

TESTED MATERIALS

For this study, two polysiloxane resins were chosen. LUKOSIL M130 – liquid methylsiloxane resin, 50 % wt. solution in xylene, viscosity 30-50 mPas (20 °C), density 1000 – 1020 kg m⁻³ and LUKOSIL 901 – liquid methylphenylsiloxane resin, 70 %wt. solution in toluene, viscosity 50- 100 mPas (20°C), density 1110 – 1150 kgm⁻³, both produced from Lučební závody Kolín, CZ.

C63 – catalyst based on alkylamines (product of Lučební závody Kolín, CZ.), was used to accelerate the polymerisation rate.

The sensitivity of threshold can be intensified by using of bipolar dopant MIMIDIOX {8-[3-(1,2-dimethylimidazolium) ethoxy-ethoxy]-3-cobalt-bis(1,2-dicarbolyde)}, molar mass 493 g/mol, prepared at the Institute of the Organic Chemistry, Prague, CZ).

MEASURING INSTRUMENTS

The instrument used for the dielectric analysis of siloxane resins indicates the changes of impedance (Z) of the measuring sensor at time, inserted in the monitored resin. The measuring sensor performs, as capacitor and is formed as printed circuit on the PTFE bed.

The resin acts as the dielectric medium in the capacitor. During networking the resin changes both its conductivity and its relative permittivity. If the measuring sensor is powered from the alternative voltage with great resistance in series, then the sensor voltage will be commensurable to its impedance. Just taken value changes of sensor voltage and its just-time phase to exciting voltage monitor the cure development of pursued resin with time. The source of current is realised with inserted the great resistor (R_s) so that it was holded R_s>Z in the range from 0.05 to 8 MΩ in ten positions.

So, for good understanding, there is important not to take exact parameters, but to find relationship between cure development of the resin and just curing temperature. Eventually, in complicated system, to monitor the influence of catalysator or some additives to resin's cure behaviour.

The measuring device consists of standard computer and its specially designed additional device. The whole device conception enables easy changing the operative programme, saving data by standard method and using the Excel programme to quick calculation of just observed data.

The operative programme is formed on basis of visualizing software Control Web 2000.

The software includes visualisation of process, data saving, printing of selected data and its transferring to Excel programme files for further data processing. Further the device enables to regulate and control temperature not to exceed the maximum temperature 350 °C. To regulate the temperature it is also possible to insert test tube with a sensor inside furnace. Temperature is observed from the three positions round the sensor.

The device contains the stabilised source of voltage +15V - -15V, switch frequency generator of alternating voltage (1, 2, 5, 10, 20 kHz), two identical channels for processing alternating voltage with outgoing rectifier and electric circuit for processing of phase. Both measuring channels – for buzz voltage and observed signal from measuring sensor have the

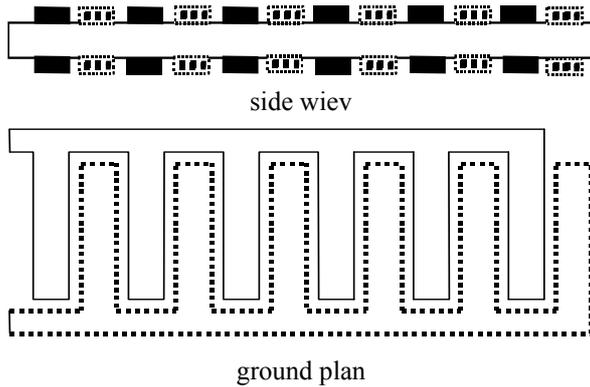


Fig. 2 Scheme of sensor

same 50Hz attenuation band on inlet filter. Measuring sensor acts as capacitor for this device. The Figure 2 shows the organisation of the sensor from the side view and the ground plan:

The pursued resin fills the gaps in the structure of printed circuit. The bed material, special PTFE - glass woven composite permits the measurement temperature up to 250 - 280 °C.

The principle of dielectric analysis is based on investigation of real part of impedance of the capacitor, changing during the cure process and it is represented by the loss of measured resistance R. This resistance can be calculated by data obtained from measuring:

$$R = \frac{U_1 R_s}{U_0 - U_1},$$

where U_0 is source voltage, R measured resistance, U_1 measuring voltage and R_s terminating resistor.

SAMPLE PREPARATION

The resin solution was applied in thin layer (max. 0.1 mm) only on one side of the sensor. The drifted sensor was left on the air to evaporate the solvent for 24 hours. Then the sensor with applied resin was put in the furnace. To prevent the contingent accidental flow of resin, the sensor was put on the PTFE plate with slots milled. The measurement was performed with selected temperature programme and R resistance were calculated. The results of measurement here are presented as dependence of the resin resistance during the time.

RESULTS AND DISCUSSION

First of all was to determine the stability of the sensor in maximal observing temperature. It was demonstrated repeatedly, that responses of the sensor at temperature 200 °C and even at 250 °C were the same therefore it was not necessary to develop some corrections for sensor responses.

REPRODUCIBILITY OF MEASUREMENT

To determine the reproducibility of measurements, these observations, the following conditions were selected: resin 901 with catalyst 1 % wt. C63, temperature up to 200 °C, heating rate 3 °C/min, current frequency 1 kHz, terminating resistor 4 MΩ. Measurement was performed twice on two different samples and it is obvious that two identical dependencies were acquired and are shown in the Fig. 3.

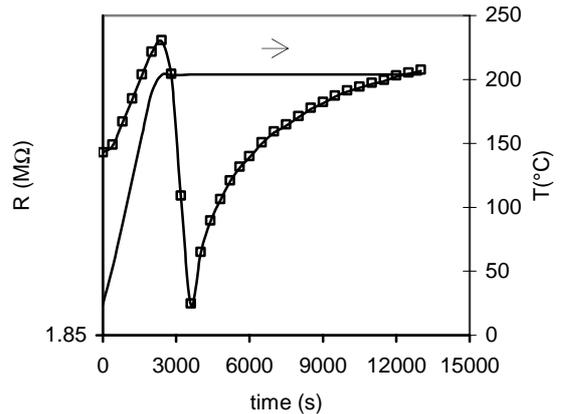


Fig. 3 Reproducibility of measurements

It is obvious from Fig. 3, that two identical dependencies were gathered. The non-monotonous dependence shows the decreasing tendency of the losing resistance, reaching minimum at 200 °C, than continuously increases with elevated temperature. Initial increase in the loss resistance reflects the influence of subsequent evaporation of the solvent. Then the following decrease of resistance is probably caused by decrease in viscosity of the system, which makes easier orientating of polarisation. After reaching the temperature 200 °C the networking starts, which causes increasing in viscosity of the system and then increasing in the loss resistance. The movement of polarized groups is more difficult. Fig. 4 shows the development of resin M 130 and resin 901 curing together with the temperature increase record.

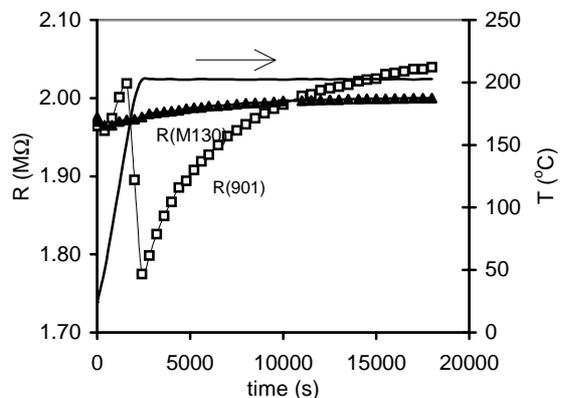


Fig. 4 Measured resistance vs. time for resins M130, 901

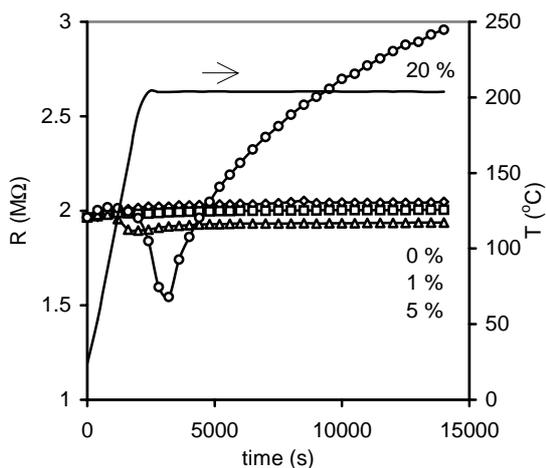


Fig. 5 Measured resistance vs. time dependence at increasing temperature and various concentration of MIMIDIOX in resin M130

Fig. 4 shows that the record covers the curing process sensitively enough for 901 resin (phenyl type) and it is in correspondence with different standard values of molar polarisation of methyl- and phenyl-groups (Chem. Abstr., 1984). Methyl groups (resin M130) are presented by low value of molar polarisation; therefore it is not possible to monitor the development of curing process by the above-mentioned method and conditions.

In case of resin M130, it was important to find a method increasing the sensitivity of response during the cure process. This problem can be solved by using dopant, which can increase the sensitivity of response of siloxane resin, for this purpose the bipolar MIMIDIOX was selected. These observations were provided under temperature increasing 3 °C/min, up to the requested temperature 200 °C, terminative resistor 4 MΩ and at frequency alternating voltage 1 kHz. A set of samples containing various concentration of MIMIDIOX: 0, 1, 5, 10 % wt were prepared. Results are shown in Fig. 5.

Results in Fig 5 confirmed our premise – with increasing concentration of MIMIDIOX response magnitude, extension increases as well during the curing process.

Then the similar dependence of resistance of M130 was obtained. The initial increase of resistance was not so obvious but with increasing temperature the loss resistance decreased (due to increasing content of MIMIDIOX it was possible to monitor the change of resistance), reaching minimum at 200 °C, when the curing process (networking) starts and movement of polarised groups decreases and the loss resistance increases with elevating temperature.

INFLUENCE OF FINAL TEMPERATURE ON THE COURSE OF CURING PROCESS

The course and rate of polycondensation polysiloxanes was pursued at constant temperature,

which is another important parameter for technologist. The method DA was verified at temperature conditions 150 °C, 200 °C, 250 °C with temperature rise 3 °C/min. Terminative resistor was 4 MΩ and frequency 1 kHz. Time of dependencies is shown in Fig. 6.

Fig. 6 shows the course of polycondensation, which is can be divided to three parts. The measured resistance initially increases due to evaporation of the rest solvent, following decrease is due to the decrease

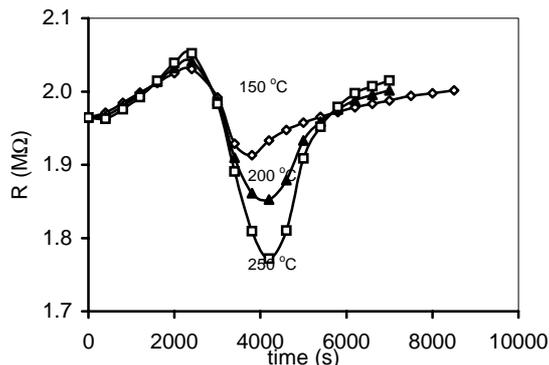


Fig. 6 Measured resistance vs. time at different temperature levels (150, 200 and 250 °C) of resin 901 + 1%wt. catalyst C63

in viscosity reaching minimum and then the networking part. Temperature 150 °C is insufficient for optimal cure. The loss resistance after reaching the requested temperature stays roughly constant. At temperature 250 °C the loss resistance decreases more than at 200 °C and following rise is steeper, too. Constant of measured resistance is reached in shorter time.

INFLUENCE OF CATALYST CONCENTRATION ON COURSE OF CURING

Investigation to the influence of catalysator concentration were carried out in terms of verification of sensitivity of the response. Blends of resin 901 with content 1, 1.5 and 2 % wt. catalyst C63 were prepared. The observations were taken under temperature rise 3 °C/min, final temperature was 200 °C, terminative resistor 4 MΩ, frequency 1 kHz.

Fig. 7 shows the running of the loss resistance with time in dependence on catalyst content of just monitored sample. The measured resistance reached minimum at 200 °C then was increasing in all samples. Only, the sample of resin 901 without catalyst showed direct increasing without preceding drop. So it follows from that observation, that curing temperature 200 °C is not sufficient.

ISOTHERMAL MEASURING

Isothermal measurement was carried out at 250 °C under conditions of terminative resistor 4 MΩ and frequency 1 kHz. In Fig. 8 is represents the record of isothermal measurement.

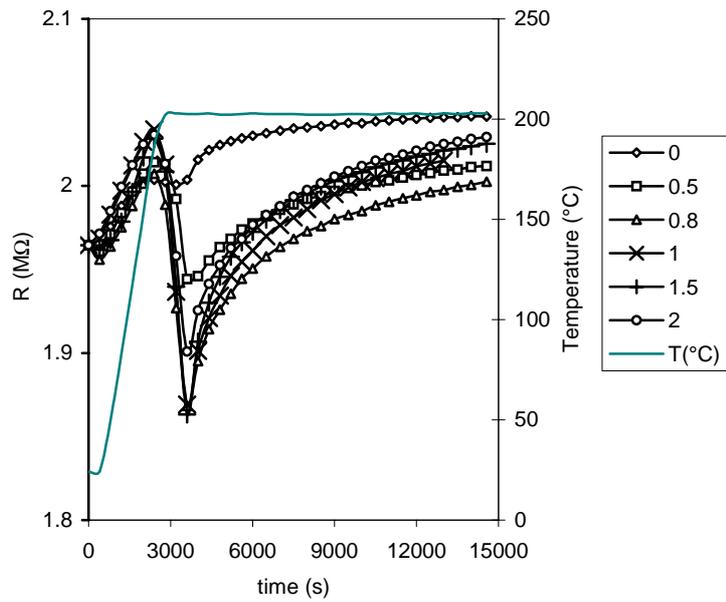


Fig. 7 Measured resistance R vs. time for different catalyst content

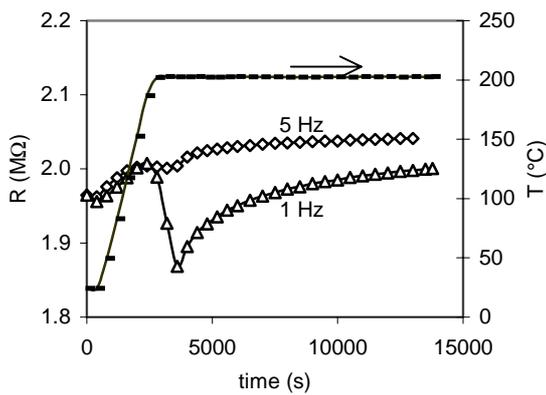


Fig. 8 Measured resistance R vs. time at isothermal condition 250°C for resin 901 + 1 %wt catal.C63

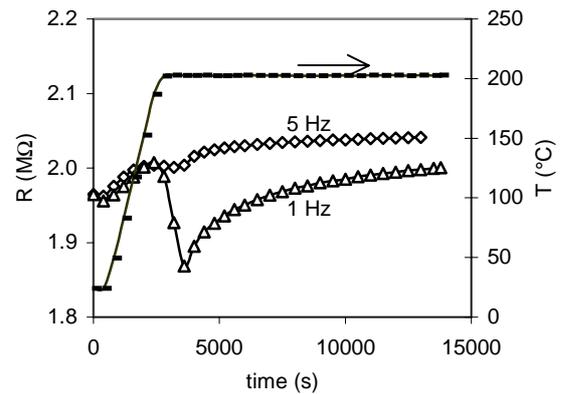


Fig. 9 Measured resistance R vs. time for resin 901+1 %wt C63 for frequencies 1 and 5 kHz

INFLUENCE OF SOURCE FREQUENCY ON SENSITIVITY OF THE RECORD

The record represented in Fig. 9 compares the time dependence of the measured resistance for frequencies 1 and 5 kHz. (Terminative resistor 4 MΩ, temperature rise 3 °C/min, final temperature 200 °C). It is obvious, that the increase in frequency of current source has reduced the sensitivity of recording.

CONCLUSION

It is possible to claim that time dependence of the measured resistance recorded siloxane resins during heat curing of can be divided into three phases – see the scheme in Fig. 10.

- 1st phase (section between points A, B) the increase in measured resistance is probably caused by either evaporation of rest solvent from resin and/or catalyst solution, or low molecular fractions of resin.
- 2nd phase (section between points B, C) the decrease of the measured resistance caused by the decrease of viscosity and fission of associated silanole group structures. Increasing concentration of catalyst increases the rate of fission.
- 3rd phase (behind point C) Dominant networking, condensation of hydroxyl groups.

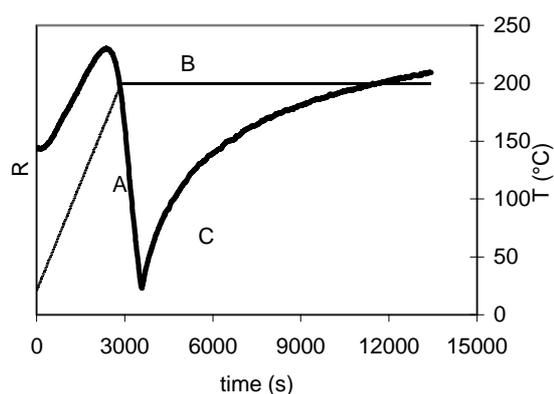


Fig. 10 Scheme of curing process

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