

## STATE OF CURE MEASUREMENTS BY DIFFERENT TECHNIQUES IN ELASTOMERIC MATRIX COMPOSITES

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### ABSTRACT

*In this study we look for: quantify the state of cure by different techniques (chemical; mechanical; thermal; spectroscopic); Comparison among the used experimental methods for measuring state of cure is made by choosing the following criteria: destructivity, need of specific sample geometry, reversion detection, error and timing; validating the numerical simulation with experimental results.; validating the numerical simulation with experimental results. As a first step test sheets were obtained from tested rubber-based compound. Different methods (DSC, NMR, mass swelling, tensile test, compression set test, relaxation, hardness, shear stress) were used to quantify the state of cure experimentally. The same techniques were applied for obtaining the state of cure in a thick part obtained from the tested compound. Then the results for the thick part were correlated with the results for the test sheets obtained by rheometer. Finally is made a comparison among the used methods by several criteria. Also numerical data obtained for evolution of state of cure in the thick part is compared by special software with the experimental data.*

**Keywords:** vulcanization, elastomer, composite, state of cure.

### INTRODUCTION

The state of cure at the end of rubber parts moulding determines the essential of the parts properties [1]. Rubber material mainly consists of long polymer chains. In the uncured state, under mechanical stress, relative chains sliding is possible: the material has a plastic behaviour. After vulcanization, in the cured state, a three-dimensional chains network is created. Chemical cross-links between the chains prevent them from relative sliding : the material has an elastic behaviour [2]. There is, therefore, a strong dependence of the mechanical properties with the cross-link density during the vulcanization process [2].

B. Bluemich [3] uses NMR and swelling methods for determining the cross-link density. In his study

he observes that with increasing curing time, cross-link density increases as the cross-linking reaction proceeds leading to a decrease in  $T_g$  and the degree of swelling. Some rubber types show reversion, i.e. a decrease in the shear modulus at high curing times due to chain scission starting to dominate cross-linking. For measuring the state of cure Richard J. Pazur [4] uses in his study several methods- NMR, tension test, swelling method, compression set and hardness tests. In our study we use a great number of methods (DSC, NMR, mass swelling, tensile test, compression set test, relaxation, hardness, shear stress) for measuring the state of cure distribution in elastomeric matrix composites.

El Labban et all [5] have developed a simulation tool that predicts and controls the temperature and the state of cure distribution within thick-section rubber

parts. The heat transfer model was experimentally validated. The curing kinetic model was validated qualitatively by the location of vulcanization front (dividing the surface between vulcanized and unvulcanized materials).

The purpose of the present paper is: to quantify the state of cure by different techniques (chemical; mechanical; thermal; spectroscopic); to compare the used experimental methods for measuring state of cure by choosing the following criteria: destructivity, need of specific sample geometry, reversion detection, error and timing; to validate the numerical simulation with experimental results.

## EXPERIMENTAL

The tested compound is natural rubber based reinforced with carbon black and sulfur vulcanized. From the compound were vulcanized two thick parts (sample A and sample B) with two different curing times giving two different state of cure distributions in the part's thickness. For characterization of the composite vulcanization properties is used rheometer type RPA2000 with moving die. The frequency is 1.66 Hz and angle 0.5° (standard setup conditions). Rheometer specimens were prepared at different temperatures (130°C, 140°C, 150°C, 160°C, 170°C). Test sheets were cured for different curing times (test sheets thickness 2mm) in order to obtain different state of cure for temperatures of 140°C and 170°C. The sheets were immediately put in ice cold water in order to freeze the state of cure. The curing temperature was measured and saved by using thermo-couples on the press form boundaries. The state of cure values of the test sheets expected by the rheometer measurements were calculated and correlated by a finite element software in order to take into consideration the increasing of state of cure during cooling. Mass swelling was carried out for 72 h until equilibrium using ambient temperature according to ISO 1817. As a solvent is used cyclohexane. The chemical cross-link density (1/2Mc) was calculated using the Flory-Rehner [5] equation. Simple stress-strain tests were made by using dynamometer and rate of 500mm/min. Compression set is measured in agreement with ISO 815-1 for 72 h and 25 % deformation. For measuring shear stress is used apparatus MetraviB for ambient temperature and frequency 5 Hz for different level of deformation. Hardness is measured by using two different methods- Shore A and IRHD. Relaxation test data

was carried out in accordance with ISO 2285 for 24 h and 200 % deformation for ambient temperature and temperature of 70°C. A wide line NMR-MOUSE (MOBILE Universal Surface Explorer) spectrometer was used to collect the relaxation data. For performing DSC-test is used apparatus DSC METTLER TOLEDO. To obtain the simulation of state of cure distribution in thickness of sample A and sample B is used special software called COMSOL.

## RESULTS AND DISCUSSION

### Comparison between different experimental methods

The normalized properties as a function of state of cure, measured by the different methods (for the test sheets) are shown in Figs. 1 and 2. The property values are increasing with the state of cure measured by the methods of hardness and the modulus. Exactly the opposite is the dependence for the values measured by the methods of NMR, DSC, compression set, relaxation and swelling. DSC and compression set are decreasing linearly. For shear modulus can be observed 3 stages- first the values of the property are rising slowly with the state of cure, after we have section with constant values and third rapid increasing of the property values, the measurements were made only for one sample for each state of cure. This must be completed with more measurements in order to have accurate results. Table 1 shows the comparison of the used methods by choosing the following criteria: destructivity, need of specific sample geometry, reversion detection, error and timing (Table 1).

From the comparison of the methods used in this study according to the chosen criteria, it is found that: all of the used methods are destructive except for NMR; DMA (shear stress) and DSC give high values of error and don't detect reversion; for relaxation and tensile test is needed a specific geometry of the specimen; NMR, mass swelling, tensile and hardness tests give reliable results for measuring the state of cure in rubber parts.

### Comparison between numerical and experimental results

The results from the comparison of the measurements obtained by using different techniques for the thick part are displayed in Figs. 3 and 4. There was also made a numerical simulation of distribution of the state of cure in the tested thick part. We have always the

Table 1. Comparison of the used methods.

Method	Destructivity	Specific sample geometry needed	Reversion detection	Error	Timing
DSC	Destructive	Not needed	Don't detects	↗	30 min
NMR	Not destructive	Not needed	Detests	↘	1min
Mass swelling	Destructive	Not needed	Detests	↘	72h
Tensile test	Destructive	Needed	Detests	↘	1 min
Compression set test	Destructive	Not needed	Don't detects	↗	72h
Relaxation	Destructive	Needed	Don't detects	↗	72h
Hardness	Destructive	Not needed	Detests	↘	1min
Shear stress	Destructive	Not needed	Don't detects	↗	3h

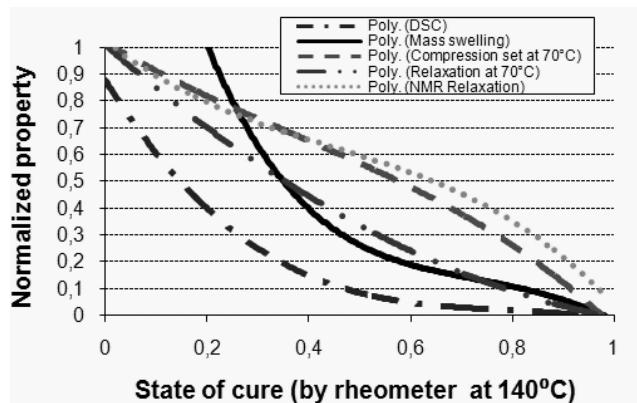


Fig. 1. Normalized properties as a function of state of cure measured by: DSC, mass swelling, relaxation, compression set and NMR tests.

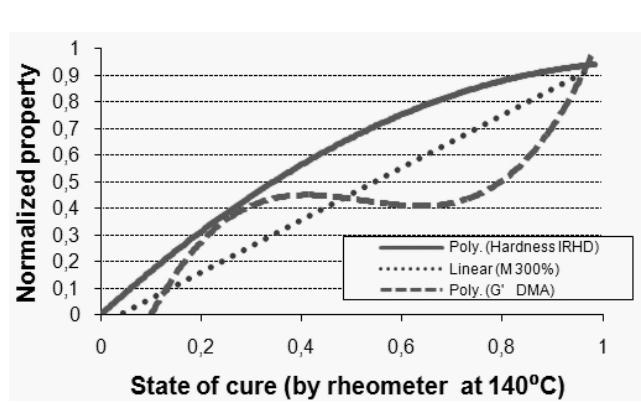


Fig. 2. Normalized properties as a function of state of cure measured by: Hardness, shear stress and tensile tests.

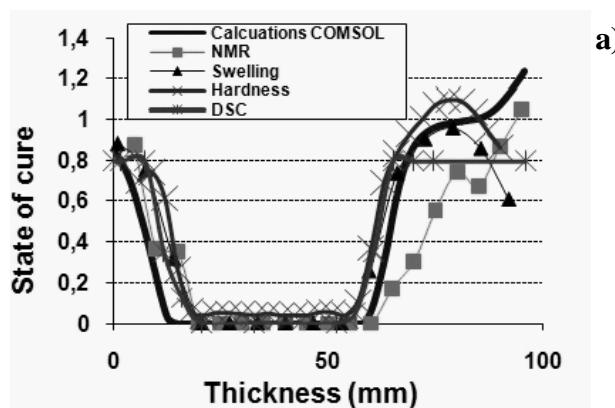


Fig. 3. Comparison between numerical and experimental results for the thick part: a) Sample A, b) Sample B.

same evolution of the curves – from the borders to the center the level of vulcanization is decreasing and unvulcanized center. In one of the borders we have reversion. In Figs. 3 and 4 is also observed that numerical

and experimental data have close values which makes the numerical prediction of distribution of state of cure reliable. The curve obtained by using swelling method has the closest values with the numerical results com-

pared to the other used methods. Unfortunately the results are obtained with different error for the different methods and it is hard to be determined which one is the most precise. But in general can be said that we have good correlation between numerical and experimental results.

## CONCLUSIONS

- Different methods (chemical, mechanical, thermal and spectroscopic) were applied successfully for measuring the state of cure in the test sheets. It is found that some of the mechanical methods (shear stress, stress-strain, compression set and relaxation) are not suitable for measuring the state of cure in thick parts but NMR, DSC, mass swelling and hardness are suitable.

- From the comparison of the methods used in this study according to the chosen criteria, it can be concluded that:

- all of used methods are destructive except for NMR;
- DMA(shear stress) and DSC gives high values of error and don't detect reversion;
- for relaxation and tensile test is needed a specific geometry of the specimen;
- NMR, mass swelling, tensile and hardness test gives reliable results for measuring the state of cure in rubber parts.

- A good correlation has been found between numerical and experimental results which give the possibility to make a reliable prediction on the distribution of state of cure in thick parts. Mass swelling method gives better results than other methods.

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