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State of cure evaluation by different experimental methods in thick rubber parts

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Properties

ABSTRACT

Purpose: The aims of this paper is to quantify the state of cure by different techniques (physico-chemical; mechanical; thermal; spectroscopic) on the thick elastomeric composites (rubber parts). An optimization is aimed from the experimental results. For this purpose, a detailed comparison is carried out with simulation for industrial applications.
Design/methodology/approach: Comparison among the used experimental methods for measuring curing phenomenon is made by choosing the following criteria: destructivity, need of specific sample geometry, reversion detection, error and timing; validation the numerical simulation with experimental results; As a first step, test sheets were obtained from the rubber-based compound. Different methods (DSC, NMR, mass swelling, tensile test, compression set test, relaxation, hardness, shear stress etc.) were used to quantify the state of cure experimentally. The same techniques were applied for evaluating 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, a comparison was carried out among the used methods by several criteria. Also numerical data obtained for evolution of state of cure in the thick parts is compared by means of special software with the experimental data.
Findings: Applications of different methods have given very successful results for measuring the state of cure in the test sheets. However, the present results showed 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 very suitable.
Research limitations/implications: Certain test such as shear stress and Dynamic Scanning Calorimetry (DSC) give high values of error and don't detect reversion. Additionally, a specific geometry of the specimen is needed for relaxation and tensile tests.
Practical implications: Certain tests such as mass swelling, tensile and hardness test give very practical and reliable results for measuring the state of cure in rubber parts in industrial applications.
Originality/value: 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 has been adapted to this research conditions and this modified test gave better results than other used methods.
Keywords: Vulcanization; Elastomeric composites; Optimization methods; Curing; Simulation

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1. 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-dimentional chains network is created. Chemical cross-links between the chains prevent them from relative sliding : the material has an elastic behaviour. There is, therefore, a strong dependence of the mechanical properties with the cross-link density during the vulcanization process [2]. Thus, the mechanical properties of the rubber depend on both the compounding and the curing process [3].

B. Bluemich [4] 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_2 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 [5] uses in his study several methods - NMR, tension test, swelling method, compression set and hardness tests. In the present study a great number of methods (DSC, NMR, mass swelling, tensile test, compression set test, relaxation, hardness, shear stress etc.) are used for measuring the state of cure distribution in elastomeric matrix composites.

El Labban et al [6] have developed a simulation tool that predicts 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). A detailed description of the models and their validation can be found in El Labban's work [6,7].

The purpose of the present paper is: to quantify the state of cure by different techniques (physico-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. Only some of the results are presented in this paper. More precisely these results have been obtained by NMR, DSC, hardness and swelling. These methods are chosen because are suitable for both test sheets and thick parts. Further examinations will be made on the relation between vulcanization and tribological properties of the samples in order to have a complete picture of the material behaviour. Some possibilities for tribological examination can be found in the work of E. Bayraktar et al [8-12].

2. Experimental procedures

The tested compound is natural rubber based reinforced with carbon black and sulphur vulcanized. From the compound were vulcanized two thick parts (sample A and sample B) with two different curing times giving two different states of cure distributions in the part's thickness. To characterise properties of the vulcanization, a rheometer (type RPA2000) with moving die was used. Standard setup conditions were chosen (frequency and angle values were taken respectively 1,66 Hz and 0,5°). Rheometer specimens were tested for examination at 4 different temperatures (130°C, 140°C, 150°C, 160°C, 170°C) during 45 minutes. Test sheets were cured for different curing times (test sheets thickness 2mm) in order to obtain different state of cure for curing temperatures 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 during the vulcanization process 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 finite element software in order to take in consideration the increasing of state of cure during cooling.

Mass swelling (Fig. 1) was carried out for 72 h until equilibrium using ambient temperature according to ISO 1817.

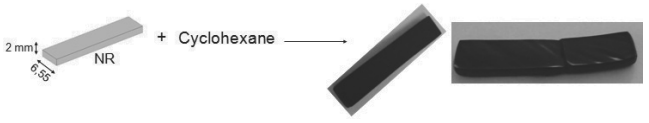


Fig. 1. Measuring state of cure by mass swelling

As a solvent, cyclohexane was used. The chemical cross-link density (1/2Mc) was calculated using the Flory-Rehner [13] equation. Three samples for each state of cure (respectively three specimens per sheet) for both vulcanization temperatures (140°C, 170°C) were measured. Hardness was measured by using two different methods- Shore A and IRHD (Fig. 2).

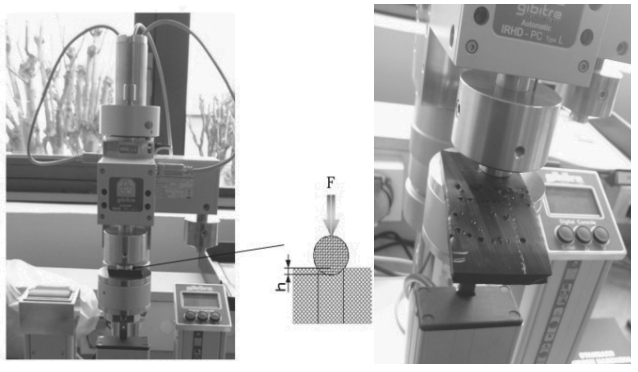


Fig. 2. Hardness measurements

A wide line NMR-MOUSE (Mobile Universal Surface Explorer) spectrometer was used to collect the relaxation data. Schematic view of The Profile-MOUSE is given in Fig. 3.

To acquire the values of enthalpy, an apparatus called "DSC METTLER TOLEDO" was used as shown in Fig. 4.

To obtain the simulation of state of cure distribution in thickness of sample A and sample B is used special software called COMSOL.

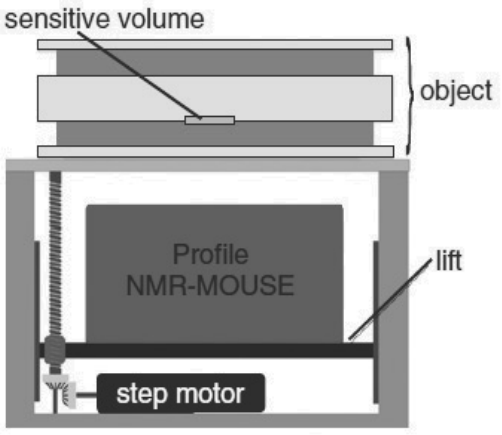


Fig. 3. Schematic view of The Profile-MOUSE

a) b)

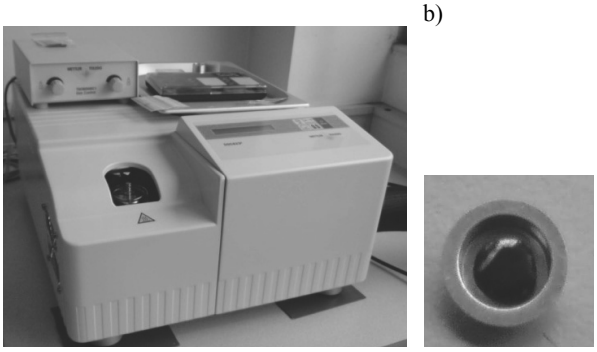


Fig. 4. a) apparatus DSC Mettler Toledo, b) geometry of the specimen

3. Results and discussion

3.1. Test sheets results

The cure characteristics of the thick parts show a noticeable pattern. First results showing the rheological behaviour of the tested compound is given for five curing temperatures in Fig. 5.

For temperatures of 130°C, 140°C and 150°C is observed a plateau behavior after approximately 15 min. It is also observed that for these temperatures there is no reversion process. For the temperatures of 160°C and 170°C the initiation period is very short, the vulcanization is very fast and the process ends with reversion and the maximum couples are higher in lower temperatures. This means that curing at high temperatures decrease the mechanical properties values. In order to obtain the state of cure (α) as a function of curing time equation (1) is used:

$$\alpha = \frac{S' - S_{min}}{S_{max} - S_{min}} \quad (1)$$

where:

S_{min}-minimum couple value,
S_{max}-maximum couple value,
S -current couple value.

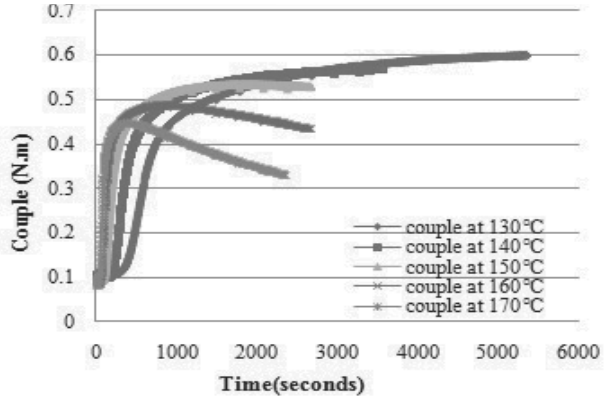


Fig. 5. Evolution of the couple for different times

After the calculations as a result is obtained the following graph:

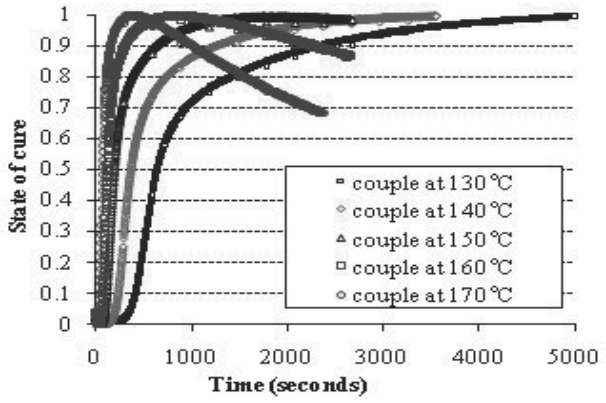


Fig. 6. State of cure evolution as a function of time

For observing the influence of curing temperature on the properties of the test sheets were chosen two temperatures - 140°C and 170°C. The particular reasons to choose these two temperatures are the following: 140°C-in order to examine the properties of the compound having plateau behavior and because of the low curing rate (it is easier to control and stop the state of cure at different level), and 170°C is chosen because for this temperature is observed reversion. Figure 6 shows the different timing in order to obtain test sheets with different level of curing. For the vulcanization temperature of 170°C, only 3 test sheets were produced (state of cure values: 0.2, 0.98 and 0.7R-reversion) because the rate of vulcanization is very high. In fact, it is very difficult to stop the process in small time intervals. For this reason, these values have been chosen in this present study.

Mass swelling results

The chemical cross-links density was measured by using mass swelling method. The average molecular mass (M_c) of the rubber chains between the cross-links was calculated using Flory-Rehner equation [13,14]. The dependence M_c as a function of state of cure is presented in Fig. 7.

For each test sheet, three specimens were measured. The points of the curves indicated in Fig. 7 represent only the average value of M_c for each state of cure (for both vulcanization temperatures).

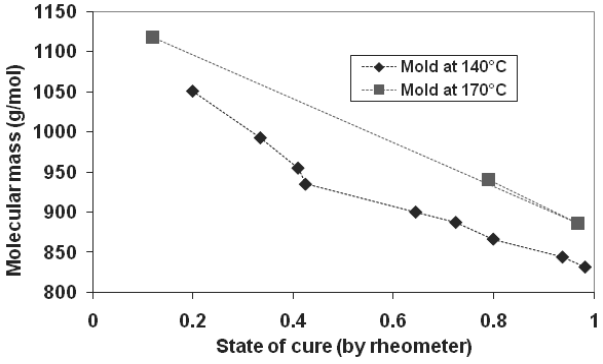


Fig. 7. Molecular mass as a function of state of cure

It is found that the values of M_c are decreasing with increasing of the level of vulcanization. For the temperature of 170°C, the highest values for both M_c and percentage of swelling are observed due to the difference in nature of the cross-links formed during the vulcanization.

In summary, the results obtained by mass swelling confirm the presence of different states of cure in the test sheets.

Hardness results

Hardness values were measured by using of Shore A and DIDC methods and the results were presented in Fig. 8.

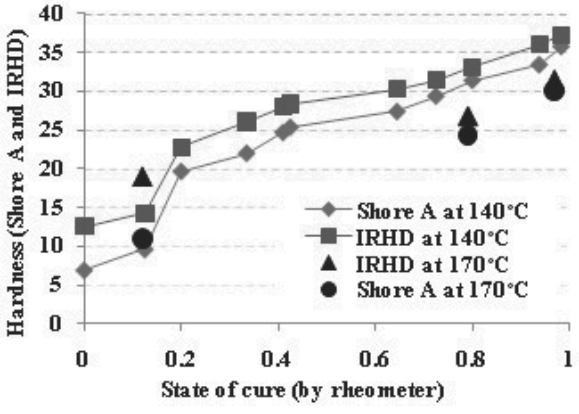


Fig. 8. Hardness as a function of state of cure

It is easy to observe from this figure that the hardness values are increasing depending on the state of cure the values. These results were similar for both of the methods used in this study. These results agree with those found in the literature. However, the values obtained with DIDC method give always higher values of hardness than those of Shore A.

A practical comparison from the results obtained for molding temperatures of 140°C and 170°C can be summarized here: hardness values found for 140°C are always higher than those for 170°C. These results are also confirmed by the couple values. It means that an increase in couple values results in augmentation in hardness value.

Differential scanning calorimetry results

DSC measurements were made in order to determine the state of cure of specimens cut from the molded test sheets (Fig. 9). The DSC method is not very sensitive for examination of composites based on natural rubber because the material gives low enthalpy values and is very difficult to be observed difference between the different levels of vulcanization. The results presented on Fig. 9 are measured with 20% of error. Because of the low sensitivity of the DSC method can be detected three levels of state of cure (S.O.C.):

S.O.C. <0,1; 0,1< S.O.C. ≤0,5; S.O.C.≥0,5.

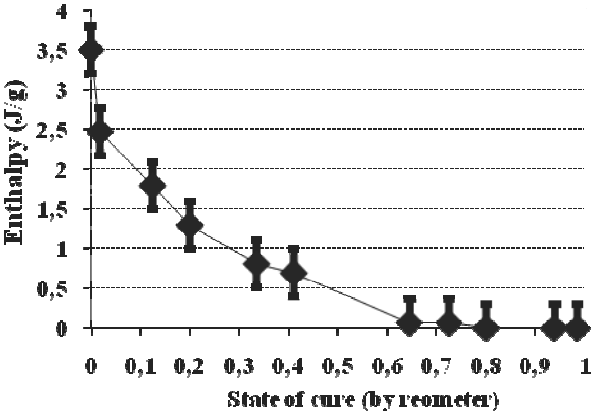


Fig. 9. Enthalpy as a function of state of cure obtained by DSC

NMR results

Three measurements were made for every state of cure of the test sheets, with error of 6%. A very good separation between NMR T_2 relaxation is observed (Fig. 10) in going from the none vulcanized through the longest cured sample indicating that the cross-link density variation exists in the test sheets. In Figure 10 is shown the comparison of the results for the test sheets molded at 140°C and 170°C.

In other words, lower values of relaxation time are observed for the samples molded at 170°C. This is due to the very high molding temperature which leads to reversion and respectively to lowering of specimens' properties.

The sample having reversion gives the lowest results. This is a phenomenon that can't be explained at this stage of our study.

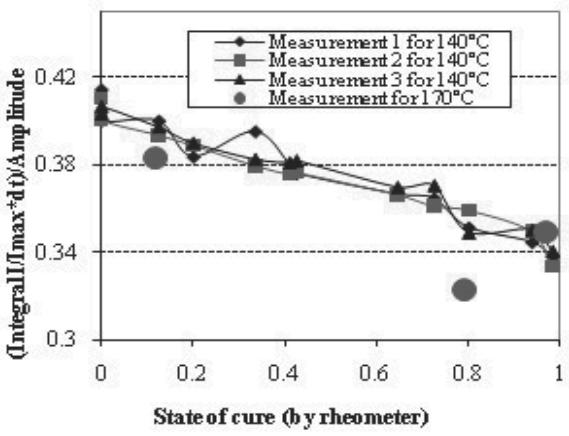


Fig. 10. (Integral I/Imax*dt)/Amplitude as a function of state of cure for molding temperatures 140°C and 170°C. T_2 relaxation refers to: T_2 = (Integral I/Imax*dt)/Amplitude

3.2. Comparison between different experimental methods

For the method of normalization for the properties, a simple equation (2) was used. The normalized properties as a function of state of cure, measured by the different methods (for the test sheets) were shown in Fig. 11a and Fig. 11b.

$$\text{Normalized value} = \frac{x - x_{min}}{x_{max} - x_{min}} \quad (2)$$

where:

x-current property value,
x_{min}- minimum property value,
x_{max}- maximum property value.

It is found that 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 the values are constant and third rapid increasing of the property values. The measurements were made only for one sample for each state of cure. Therefore the results must be confirmed with more experimental data.

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.

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.

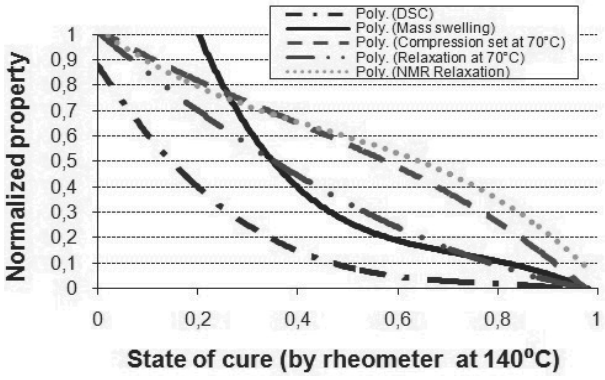


Fig. 11a Normalized properties as a function of state of cure measured by: DSC, mass swelling, relaxation, compression set and NMR tests respectively

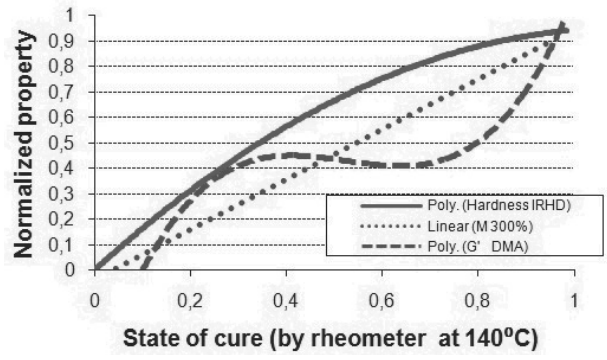


Fig. 11b. Normalized properties as a function of state of cure measured by hardness, shear stress and tensile tests

In most rubber manufacturing works, curing time of thick rubber components is carried out more and less with trial and error and/or they work on their manufacturing experiences that they have very rich knowledge.

Even with either of the above methods that we have experienced in the frame of this research, the extreme curing time is for all time engaged to ensure that the rubber is properly cured throughout the whole bulk of the pieces. For this reason, curing time should be optimized by using a correct modelling and real simulation with FEA technique. By this way, the curing time can be shortened for increasing the productivity of the manufacturing without defect.

In addition to the thermal problems mentioned above, significant variations can occur from batch to batch in the preparation of the compounded rubber or other elastomeric substance. Moreover, there can be variations in heat transfer characteristics between different moulds employed for curing of the same type piece.

Table 1.
Comparison of the used methods

Method	Destructivity	Specific sample geometry needed	Reversion detection	Error	Timing
DSC	Destructive	Not needed	Doesn't detect	High	30 min
NMR	Not destructive	Not needed	Detects	Low	1 min
Mass swelling	Destructive	Not needed	Detects	Low	72 h
Tensile test	Destructive	Needed	Detects	Low	1 min
Compression set test	Destructive	Not needed	Doesn't detect	Low	72 h
Relaxation	Destructive	Needed	Doesn't detect	Low	24 h
Hardness	Destructive	Not needed	Detects	Low	1 min
Shear stress	Destructive	Not needed	Doesn't detect	High	3 h

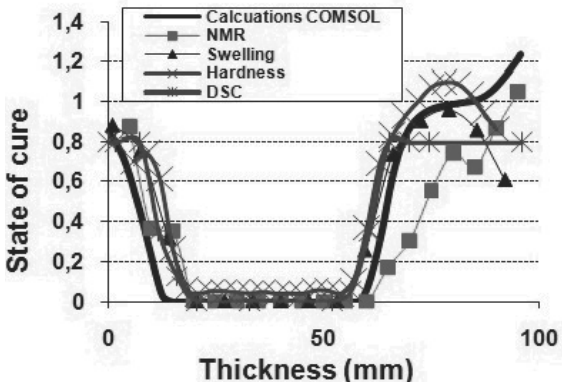
It should be noted that, due to low thermal conductivity, heat in the rubber is also dissipated very slowly to the environment (air) during the cooling step. The rubber is thus cooled down very slowly. Curing of the rubber compounds, particularly in the inner area where the temperature reduction takes place very slowly, could therefore still occur at this step. Comparison of the contour plots of cure distribution obtained before and after the cooling step reveals that the cure level increases significantly during the cooling step. It should be noted that the degree of curing taking place during the cooling step depends strongly on cure behaviour (for example; scorch time, optimum cure time and cure rate) of the sample.

In this case, interesting results have been found by S. Pongdhorn and U. Thepsuwan [15]. They have shown that despite the apparent simplicity of the experiment and the simulation, there are sources of potential error, most importantly in the modelling. As far as the simulation is concerned, transient thermal behaviour, in which the temperature at any point within a body varies with both time and position, is controlled by the thermal diffusivity of the material involved. Thus the prediction accuracy depends greatly upon the accuracy of thermal conductivity, specific heat and density of material. During transient thermal analyses, it was assumed that both density and thermal conductivity are independent of temperature over the range 23-150°C. Naturally, these properties can be function of not only the temperature but also of the state of cure.

3.3. 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 Fig. 12a and Fig. 12b. There was also made a numerical simulation of distribution of the state of cure in the tested thick parts. The evolution of the curves is always the same - from the borders to the centre the level of vulcanization is decreasing and the centre always stays not yet vulcanized. In one of the borders, different reversion phenomena can occur. This is probably due to high curing temperature and also due to heat of chemical reaction that is very important during vulcanization in the centre of the part. These phenomena can also be observed in Figures 12a and 12b respectively. In these figures, numerical and experimental data have been indicated for the simple comparison.

a)



b)

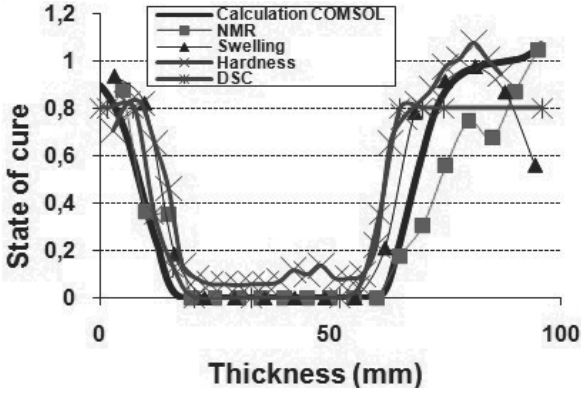


Fig. 12. Comparison between numerical and experimental results for the thick part: a) Sample A, b) Sample B

These values are very close each other: It means that the numerical prediction for the distribution of state of cure reliable. The curve obtained by using swelling method is quasi the same with that of the numerical results regarding to the other methods used in this study. However, 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, as an general can be said that there is a good correlation between numerical and experimental results.

In fact, for practical applications, it is optional that, for production of large articles such as tires, only and only 25-35% cure at internal area may be induced whilst in the mould as the cure level will increase during the cooling step or post cure period utilizing the residual heat. Nevertheless, it should be bear in mind that the curing at this point must be sufficient to prevent distortion of product shape and some other internal defects such as cavities and also porosity that caused by dissolved gases, once the external pressure is removed.

4. Conclusions

Some practical conclusions can be driven from this research:

- Different methods (physico-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 used methods.

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References

[1] A. Cheymol, Processing of elastomers, Hermes - Lavoisier, 2006.
[2] F. Dimier, Injection of reactive systems: kinetic and rheological properties (Injection des systèmes réactifs: détermination de lois cinétiques et rhéologiques et modélisation), ENSMP, PhD Report, 2003 (in French).
[3] Sh. Nozu, H. Tsuji, M. Itadani, W. Fujiwara, K. Ohnishi, Study of cure process of thick solid rubber, Journal of Materials Processing Technology 20/1 (2008) 720-724.
[4] B. Blumich, J. Perlo, F. Casanova, Mobile single-sided NMR, Progress in Nuclear Magnetic Resonance Spectroscopy 52 (2008) 197-269.
[5] R.J. Pazur, F.J. Walker, State of cure measurements in peroxide and sulfur cured, Proceedings of the Fall 174th Technical Meeting of the Rubber Division of the American Chemical Society 14-16 (2008) 1547-1977.
[6] A. El Labban, P. Mousseau, R. Deterre, J.-L. Bailleul, A. Sarda, Temperature measurements and control within molded rubber during vulcanization process, Elsevier Ltd., 2009.
[7] A. El Labban, Optimisation of cure cycle of a piece moulded in elastomers, PhD Report, University of Nantes, 2008.
[8] R. Luong, N. Isac, E. Bayraktar, Failure mechanisms in thin rubber sheet composites under static solicitation, Journal of Achievements in Materials and Manufacturing Engineering 2/1 (2007) 43-46.
[9] T.D. Silva Botelho, E. Bayraktar, Experimental and numerical study of damage initiation mechanism in elastomeric composites, Journal of Achievements in Materials and Manufacturing Engineering 36/1 (2009) 65-70.
[10] D.M. Bieliński, O. Dobrowolski, P. Głąb, L. Ślusarski, Filler dispersion and associated tribological properties of rubber, Proceedings of the 13th International Scientific Conference "Achievements in Mechanical and Materials Engineering" AMME'2005, Gliwice-Wisła, 2005, 30-34.
[11] T. Da Silva Botelho, N. Isac, E. Bayraktar, Modelling of damage initiation mechanism in rubber sheet composites under the static loading, Journal of Achievements in Materials and Manufacturing Engineering 22/2 (2007) 55-58.
[12] D.M. Bieliński, P. Głąb, L. Ślusarski, New approach to study tribological properties of polymer materials. A case of car windshield wipers, Journal of Achievements in Materials and Manufacturing Engineering 15 (2006) 71-78.
[13] N.A. Neuburger, B.E. Eichinger, Critical experimental test of the Flory-Rehner theory of swelling, Macromolecules 21 (1988) 3060-3070.
[14] C.V. Marykutty, E.J. Mathew, S. Thomas, Studies on a new binary accelerator system in sulfur vulcanization of natural rubber, Elastomers and Plastics (2008) 383-389.
[15] S. Pongdhorn, U. Thepsuwan, Prediction of cure level in thick rubber cylinder using finite element analysis, Science Asia 28 (2002) 385-391.