

Merjenje točke poroznosti v gumi

Measurement of the Point of Porosity in Rubber

UROŠ ILIĆ - IVAN BAJSIĆ

Vulkanizacija surovca v stiskalnici zahteva poznavanje temperaturnih in tlachnih polj v surovcu in v okolini ogrevanega surovca avtomobilske pnevmatike. Ker je surovec sestavljen iz različnih gumenih zmesi z različnimi vulkanizacijskimi lastnostmi, je treba vedeti, kdaj je surovec na najbolj kritičnem mestu dovolj vulkaniziran, da ga lahko vzamemo iz stiskalnice in da sestavnii deli iz različnih zmesi kljub zmanjšanju tlaka ostanejo homogeni. Prispevek prinaša prikaz nove metode za določitev najmanjše vulkaniziranosti zmesi in določitev vpliva najpomembnejših fizikalnih veličin, ki bodo pri meritvi najmanjše vulkaniziranosti zmesi povzročale največje sistemskie in naključne merilne pogreške. Prispevek za obravnavani primer izračuna prikazuje povezavo med izmerjeno najmanjšo vulkaniziranostjo in izmerjenimi reološkimi lastnostmi zmesi.

Ključne besede: guma, meritve temperature, poroznost, metode numerične

The vulcanization of a green tyre in a press requires knowledge of temperature and pressure fields in the heated up green tyre itself and its surroundings as well. Due to the fact that each green tyre is composed of different rubber compounds with different vulcanization properties one should know when the most critical spot of a green tyre is vulcanized enough so that the tyre can be removed from a press and the components of different compounds remain homogenous despite the reduced pressure. The paper describes the new method for determination of the minimum level of compound vulcanization and defines the influence of the most important physical values which will cause the greatest systematic and random measurement errors when measuring the minimum of vulcanization. The example presented shows the connection between the measured minimum vulcanization level and the measured rheologic properties of a compound.

Key words: rubber, temperature measurement, porosity, numerical method

0 UVOD

Postopek vulkanizacije se prične v vulkanizacijski stiskalnici, kjer v surovcu s sprememboto temperature in tlaka sprožimo proces vulkanizacije. Uspešno je surovec vulkaniziran takrat, ko je na najbolj kritičnem mestu dovolj vulkaniziran, na najmanj kritičnem delu pa ni preveč vulkaniziran. Stopnjo pravšnje vulkaniziranosti dela zmesi surovca, ki poteka pod tlakom v stiskalnici, ocenimo z merjenjem točke poroznosti. S predstavljenim metodo določitve točke poroznosti določimo najmanjšo stopnjo vulkaniziranosti zmesi, ki se uporablja za potniške in tovorne avtomobilske pnevmatike.

1 VULKANIZACIJSKI UČINEK

Koncentracija kemičnih vezi v zmesi se spreminja glede na čas izpostavljanja določeni temperaturi in s temperaturo zmesi. Predpostavimo, da popiše spreminjanje koncentracij kemičnih vezi v zmesi kemična reakcija prvega reda. S spremenljivko x zapišimo razmerje med trenutno in največjo koncentracijo kemičnih vezi v zmesi:

$$x = \frac{c(t)}{c(\text{maks.})}$$

0 INTRODUCTION

The vulcanization process begins in a vulcanization press where by a change of temperature and pressure in a green tyre a vulcanization process is induced. The green tyre is sufficiently vulcanized when its most critical spot is adequately vulcanized and its least critical spot not undervulcanized. The appropriate vulcanization degree of the part of a green tyre compound, which is performed under pressure in the press, is estimated by measuring the point of porosity. With the presented method for determination of the point of porosity the minimum degree of vulcanization of a compound being used for passenger car tyres and truck tyres is determined.

1 VULCANIZATION EFFECT

The change of the concentration of chemical bonds in a compound is conditioned both by the time of exposure to a certain temperature and by the temperature of a compound. It is assumed that the change of the concentration of chemical bonds in a compound is a chemical reaction of the first order. The variable x is used to describe the relation between the momentary and the maximum concentration of chemical bonds in a compound:

$$\frac{dx}{dt} = k(T)(1 - x) \quad (1)$$

Hitrost kemične reakcije v zmesi popišemo z Arrheniusovo diferencialno enačbo v naslednji obliki:

$$\frac{d(\ln k)}{dT} = \frac{A}{RT^2} \quad (2)$$

Z rešitvijo enačbe (2) z običajno integracijsko metodo in vstavljivijo v enačbo (1) dobimo:

The speed of chemical reaction in a compound is noted by the Arrhenius differential equation:

$= \frac{1}{RT^2}$ (2) the individual progress guideline, a clearly make the objectives regarding the level

By solving the equation (2) by means of the

By solving the equation (2) by means of the common integration method and inserting into the equation (1), the following result is obtained:

$$EM(t) = K \int_{x_0}^x \frac{dx}{(1-x)} = K \int_{t_0}^t e^{\frac{A}{R}\left(\frac{1}{(g_0+273,15)} - \frac{1}{T(t)}\right)} dt = K \int_{t_0}^t VE(t) dt \quad (3).$$

2 DOLOČITEV NASTALE TOPLOTE V ZMESI

Do nastajanja toplote v zmesi, ki jo segrevamo, prihaja zaradi faznih prehodov (taljenje, kristalizacija itn.) ali kemičnih reakcij (vulkanizacija, oksidacija, degradacija). Z diferencialnim kalorimetrom smo različnim zmesem z različnimi spremembami (dinamično segrevanje, izotermno segrevanje pri 160°C in 210°C) določili celotno nastalo toploto med preizkusi. Pri tem smo predpostavili, da tudi med vulkanizacijo surovca v stiskalnici nastaja v zmesi surovca podoben del toplotne energije [10], [11].

Vzorec mase 50 mg smo pri dinamičnem preizkusu zaprli v jeklen lonček v dušikovi atmosferi (N_2) in ga segrevali v toku dušika (N_2) s hitrostjo 20 °C/min v temperaturnem območju od 30 °C do 300 °C. Komponenta dinamičnega merilnega pogreška je zaradi majhne časovne konstante vzorca v primerjavi s časom trajanja preizkusa minimalna.

Za izotermni preizkus na 160 °C in 210 °C smo vzorce pripravili enako kakor v primeru dinamičnega preizkusa, le da smo v tem primeru segrevali dva vzorca. En vzorec je bil že vulkaniziran, drugi pa ne. Razlika med dovedenimi toplotami prikazuje endotermne in eksotermne procese v vzorcu. Hitrost segrevanja vzorcev je bila 80 °C/min za izotermni preizkus pri 160 °C in 500 °C/min za izotermni preizkus pri 210 °C.

Vrednotenje izmerkov dinamičnih preizkusov je težavno, ker je težko oceniti začetek in konec eksotermnih in endotermnih procesov ter lego bazne črte (črta preizkusa brez nastajanja topote zaradi kemičnih reakcij). V vseh preizkusih smo ugotovili, da so endotermni procesi zanemarljivi v primerjavi z eksotermnimi.

2 DETERMINATION OF GENERATED HEAT IN A COMPOUND

The heat in a compound being heated is generated by a phase change (melting, crystallization, etc.) or by chemical reactions (vulcanization, oxidation, degradation). By means of a differential calorimeter we determined the entire heat generated during the experiments for different compounds with different changes (dynamic heating, isothermal heating at 160 °C and 210 °C). We presumed that also during the vulcanization of a green tire in a press, a similar portion of heat energy is being generated in the green tire compound [10], [11].

When carrying out the dynamic test a sample of mass of 50 mg was placed and closed in a steel pot in nitrogen atmosphere (N_2) and heated in nitrogen flow (N_2) with a speed of 20 °C/min at a temperature range from 30 °C to 300 °C. The component of a dynamic error of measurement is minimal owing to the low sample time constant if compared to the duration of the experiment.

The samples for the isothermal test at 160 °C and 210 °C were prepared in the same way as those for the dynamic test, the difference being that in the second test two samples were heated. One sample was already vulcanized and the other one not. The difference between heats supplied shows the endothermic and exothermic processes in the sample. The speed of heating was 80 °C/min for the isothermal test at 160 °C, and 500 °C/min for the isothermal test at 210 °C.

The evaluation of dynamic test measurements is not simple, for it is difficult to estimate the beginning and the end of the exothermic and endothermic processes and the position of the basis line (test line without generating heat due to chemical reactions). On the basis of the experiment performed we found that endothermic processes are negligible if compared to exothermic ones.

Preglednica 1: S preizkusi določene celotne specifične entalpije zaradi kemičnih reakcij
Table 1: Total specific enthalpies due to chemical reactions determined by tests

vzorec sample	dinamični preizkus dynamical test J/g	izotermni preizkus isothermal test 160 °C J/g	izotermni preizkus isothermal test 210 °C J/g
zmes 22475 compound 22475	od -10,4 do -10,2	- 7,5	- 6,0
preizkušana zmes tested compound	od -7,1 do -6,8	/	/

V primeru izotermnega preizkusa smo dobili manjše celotne specifične reakcijske entalpije, ker smo morali surovca segreti od 30 °C na 160 °C ozziroma 210 °C. Ker je nemogoče stehtati popolnoma enake vzorce, je k izračunani celotni reakcijski entalpii prištet tudi dinamični merilni pogrešek zaradi masne neenakosti vzorcev. Upoštevati je tudi treba, da so vzorci relativno majhni in je vpliv nehomogenosti vzorcev vreden upoštevanja.

3 TOČKA POROZNOSTI

Točka poroznosti je izobarni čas vulkanizacije, ki ga dobimo na podlagi izmerjenega ali kako drugače določenega poteka temperature na mestu nastajanja najmanjšega mehurja v zmesi. Mejna vrednost je dosežena, ko se molekularno zamreženje na določenem mestu izvede do takšne stopnje, da matrika zmesi zdrži parni tlak hlapov, ki nastajajo zaradi sprevanja zmesi.

Osnadnji problem preizkusa je zagotoviti enakomeren tlak, ki se lahko spreminja prav enako ali manj, kolikor se spreminja tlak notranjega ogrevanja pri vulkanizaciji surovcov. Ta problem se prevede na konstrukcijo kalupa in spremjanje vira tlaka (oljna črpalka).

4 FIZIKALNI MODEL KALUPA

Na podlagi določenih vzorcev in narejenih kalupov smo zgradili dva fizikalna modela (model kocke in model zagozde). Z obema modeloma smo želeli določiti vpliv robnih in začetnih pogojev na spremjanje temperature v merjencu (zagozdi ali kocki) ob predpostavki homogenega nastajanja topote v merjencu. Slika 1 prikazuje model zagozde, slika 2 model kocke.

In the case of the isothermal test minor total specific reaction enthalpies appeared which is due to the fact that the green tyre had to be heated from 30 °C to 160 °C and 210 °C respectively. Since it is not possible to weigh the samples so to as be completely equal, the dynamic error of measurement due to the mass inequality of samples should be added to the calculated total reaction enthalpy. It should be taken into account that the samples are relatively small and the influence of inhomogeneity of samples is quite considerable.

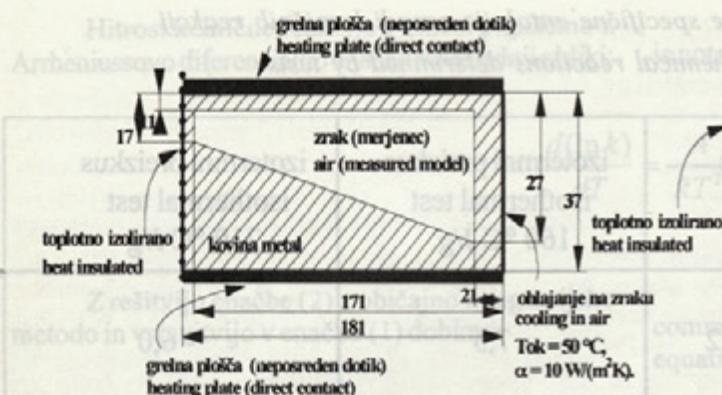
3 POINT OF POROSITY

The point of porosity is the isobaric vulcanization time obtained on the basis of a measured - or in some other way determined - course of temperature on the spot where the minimum bubble in a compound is formed. The limiting value is reached when molecular cross linking on a certain spot is performed to the degree at which the matrix of a compound withstands the steam pressure of vapours which are formed due to compound heating.

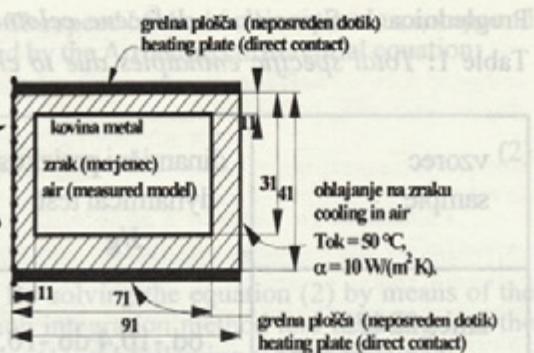
The main problem of the experiment is how to ensure a constant pressure which can be changed to an equal or lesser degree compared to the pressure of inner heating when vulcanizing green tyres. The problem lies in the mould design and change of the pressure source (oil pump).

4 PHYSICAL MODEL OF A MOULD

Based on certain samples and already made moulds, we have built two physical models (a model of a cube and a model of a wedge). Both models served to determine the influence of boundary and initial conditions on temperature changes in the measured model (a wedge or a cube) under the supposition that the heat in the measured model is generated homogeneously. Figure 1 shows the model of a wedge and the Figure 2 the model of a cube.



Sl. 1. Model kalupa 1
Fig. 1. Mould model 1



Sl. 2. Model kalupa 2
Fig. 2. Mould model 2

Model zagozde (model kalupa 1) in model kocke (model kalupa 2) ustrezata prerezu kalupa, ki smo ga uporabljali za preizkušanje točke poroznosti po modelu zagozde in kocke. V obeh primerih smo predpostavili temperaturo zgornje grelne plošče 150,5 °C za ves čas trajanja preizkusov. Za izračun toplotne prestopnosti α smo predpostavili naravno konvekcijo toplote s površine s temperaturo 148,5 °C na 50 °C [1]. Za oba modela smo upoštevali simetričnost kalupa.

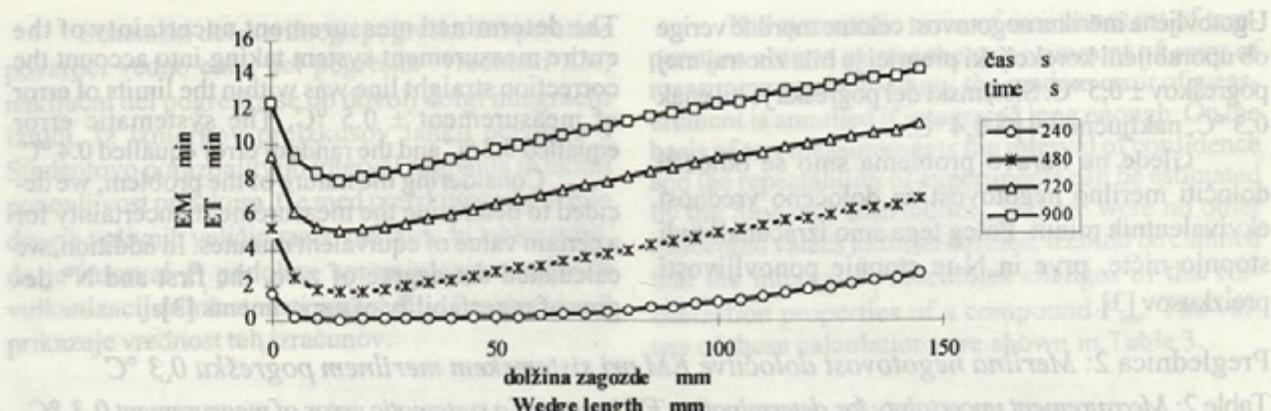
5 REZULTATI NUMERIČNEGA MODELIRANJA

Z metodo končnih razlik smo izračunali časovno spremenjanje temperature kalupa 1 in kalupa 2 za koračno spremembo temperature na robu [4], [5], [7] in [8]. Ta izračun ustreza dejanskemu ogrevanju kalupa z zagozdo in s kocko. Drugi del izračuna naj bi prikazal spremenjanje temperature gumene zagozde in kocke s temperaturo 22 °C (merjenca), ki ga vstavimo v segret kalup. Izračun je bil narejen za merjenec brez nastajanja toplote in za merjenec z enakomernim homogenim nastajanjem toplote v zagozdi in kocki od 80 °C do 140 °C. Namen teoretičnega izračuna je bil pokazati, kolikšen merilni pogrešek napravimo, če merilnega zaznavala ne vstavimo v naprej določeno mesto merjenca, ampak v okolico tega mesta. Na podlagi teoretičnih izsledkov smo dobili linearne korekcijske enačbe sprememb EM (ekvivalentnih minut) zaznaval, ki so geometrijsko odstopala od želenega mesta v merjencu.

The model of a wedge (mould model 1) and the model of a cube (mould model 2) correspond to the mould cross section which has been used for testing the point of porosity based on the models of a wedge and a cube. In both cases we assumed the temperature of the upper heating plate to be 150.5 °C during the total duration of experiments. To calculate the heat convection coefficient α we assumed the natural heat convection from a surface with temperature to be 148.5 °C to 50 °C [1]. For both models the symmetry of the mould has been taken into account.

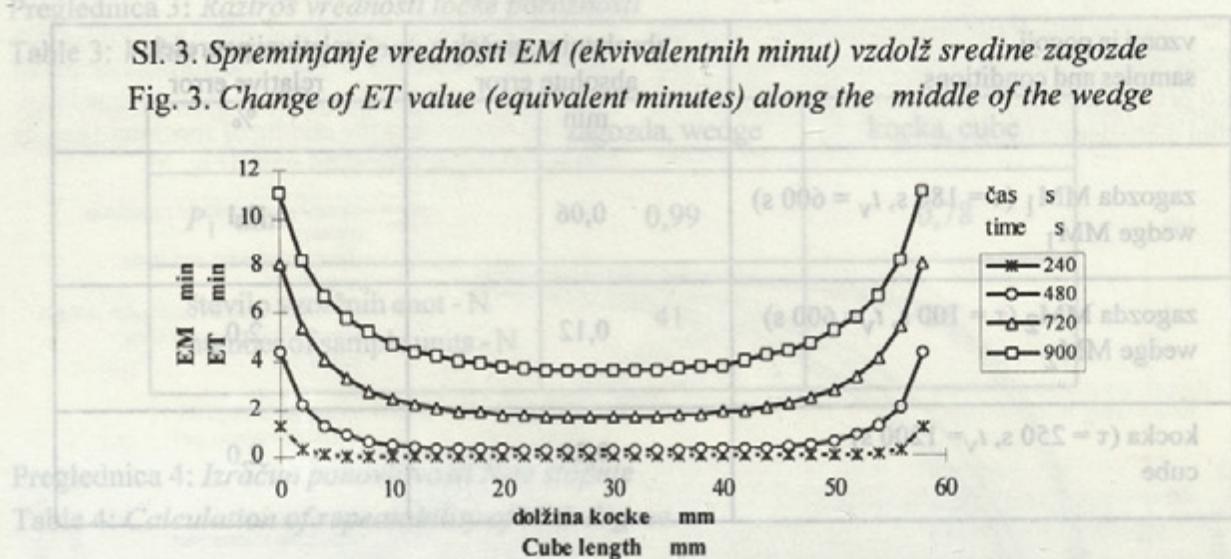
5 RESULTS OF NUMERICAL MODELLING

Using the method of finite differences, a time change of temperature of mould 1 and mould 2 for step input of temperature on the boundary was calculated [4], [5], [7], and [8]. The calculation corresponds to the actual heating of a mould for a wedge and a cube. With the second part of the calculation a change of temperature of a rubber wedge and a cube with temperature of 22 °C (specimen) should be shown, which is to be inserted in a heated mould. The calculation was made for a specimen without the heat generation and for a specimen with the uniform heat generation in the wedge and the cube from 80 °C to 140 °C. The purpose of the theoretical calculation was to show what error of measurement can occur if a sensor is not inserted exactly into a previously prepared spot in a specimen but into the surrounding of this spot. Based on theoretical results of the research we obtained linear correction equations of changes the ET values (equivalent minutes) for sensors which geometrically differ from the desired spot in the specimen.



Sl. 3. Spreminjanje vrednosti EM (ekvivalentnih minut) vzdolž sredine zagozde

Fig. 3. Change of ET value (equivalent minutes) along the middle of the wedge



Sl. 4. Spreminjanje vrednosti EM (ekvivalentnih minut) vzdolž sredine kocke

Fig. 4. Change of ET value (equivalent minutes) along the middle of the cube

Slika 3 in 4 prikazujejo izračunano vrednost spremenjanja EM v modelu kalupa 1 - zagozde in modelu kalupa 2 - kocke. Na podlagi prikazanih rezultatov s slike 3 vidimo, da se po sredini zagozde od 25 mm do 135 mm vrednost EM spreminja linearno. Slika 4 prikazuje velikost merilnega pogreška, če temperaturno zaznavalo ni postavljeno na geometrijsko sredino kocke. Podobne rezultate dobimo za spremenjanje EM navpično po sredini kocke. V legendi slik 3 in 4 je naveden čas od vstavitve merjencev v kalup.

Figures 3 and 4 show the calculated value of a change of ET in mould model 1 - a wedge and mould model 2 - a cube. On basis of the results presented in the Figure 3 one can see that along the middle of the wedge from 25 mm to 135 mm the value of ET changes linearly. Figure 4 shows the size of error of measurement, if a temperature sensor is not placed at the geometric centre of the cube. Similar are the results for changes of ET vertically along the middle of the cube. The explanation of Figures 3 and 4 shows the time after the insertion of a specimen into the mould.

6 EXPERIMENTS

V dveh točkah pri merjencu v obliki zagozde in drugem merjencu v obliki kocke smo izmerili temperaturo s termopari Fe-CuNi (tip J). Nastali meritni signal smo prek sistema za zbiranje podatkov in A/D pretvornika shranili na osebni računalnik [2], [6] in [9]. Poprej smo celotno meritno verigo umerili z referenčnim termometrom.

In a specimen in the form of a wedge the temperature was measured at two points and at one point in the specimen formed as a cube. The temperature was measured by thermocouples Fe-CuNi (type J). The generated measuring signal was through the system for data acquisition and A/D converter was stored into PC [2], [6], and [9]. Before that the entire measuring system was calibrated by a reference thermometer.

Ugotovljena merilna negotovost celotne merilne verige ob uporabljeni korekcijski premici je bila znotraj mej pogreškov $\pm 0,5^{\circ}\text{C}$. Sistemski del pogreška je bil enak $0,3^{\circ}\text{C}$, naključni del pa $0,4^{\circ}\text{C}$.

Glede na naravo problema smo se odločili določiti merilno negotovost za določeno vrednost ekvivalentnih minut. Poleg tega smo izračunali tudi stopnjo ničte, prve in N -te stopnje ponovljivosti preizkusov [3].

Preglednica 2: Merilna negotovost določitve EM pri sistemskem merilnem pogrešku $0,3^{\circ}\text{C}$

Table 2: Measurement uncertainty for determination ET in case of a systematic error of measurement $0,3^{\circ}\text{C}$

vzorci in pogoji samples and conditions	absolutni pogrešek absolute error min	relativni pogrešek relative error %
zagozda MM ₁ ($\tau = 180\text{ s}$, $t_v = 600\text{ s}$) wedge MM ₁	0,06	2,1
zagozda MM ₂ ($\tau = 100\text{ s}$, $t_v = 600\text{ s}$) wedge MM ₂	0,12	2,0
kocka ($\tau = 250\text{ s}$, $t_v = 1200\text{ s}$) cube	0,20	2,0

Preglednica 2 prikazuje merilno negotovost določitve EM pri sistemskem merilnem pogrešku $0,3^{\circ}\text{C}$, predpostavljenem eksponentnem temperaturnem odzivu s temperature 30°C na 151°C , kjer je τ časovna konstanta eksponentnega temperaturnega odziva in t_v čas vulkanizacije pod tlakom. Z označbo MM smo označili geometrijsko mesto postavitve zaznavala v merjencu.

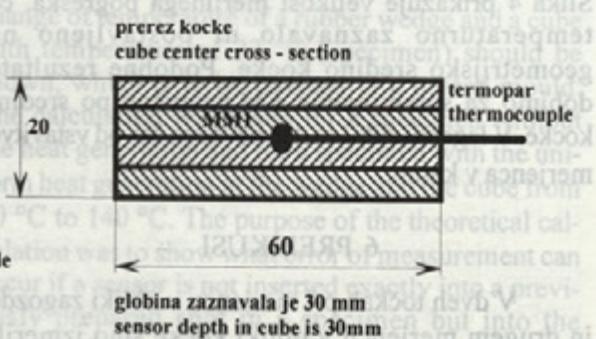
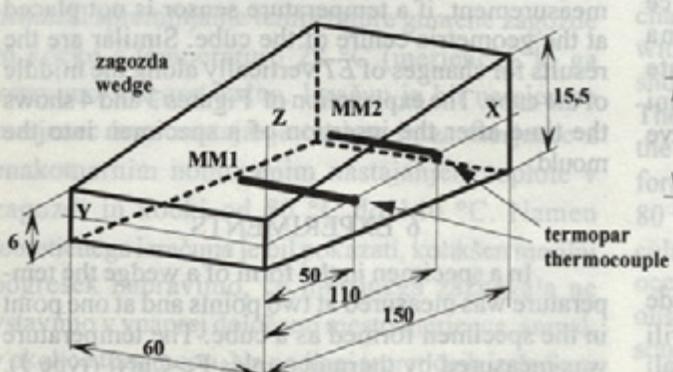
Na sliki 5 je prikazana namestitev zaznavala v zagozdi in kocki kot merilno mesto - MM.

The determined measurement uncertainty of the entire measurement system taking into account the correction straight line was within the limits of error of measurement $\pm 0,5^{\circ}\text{C}$. The systematic error equalled $0,3^{\circ}\text{C}$ and the random error equalled $0,4^{\circ}\text{C}$.

Considering the nature of the problem, we decided to determine the measurement uncertainty for a certain value of equivalent minutes. In addition, we calculated the degree of zero, the first and N^{th} degree of repeatability of experiments [3].

Table 2 shows the uncertainty of measurement of ET determination in case of a systematic error of measurement $0,3^{\circ}\text{C}$, taking into account a temperature response from temperature of 30°C to 151°C , where τ is a time constant of the exponent temperature response and t_v is vulcanization time under pressure. By the designation MM the geometric spot for placing the sensor into the specimen was marked.

Figure 5 shows placing of sensors in the wedge or the cube as a measurement point - MM.



Sl. 5. Namestitev merilnih zaznaval v zagozdi in kocki

Fig. 5. Placing of measurement sensors in the wedge or the cube

Sistemski del merilnega pogreška temperature povzroči vedno enak del pogreška vrednosti EM , naključni del pogreška se ob dovolj dolgi integraciji izniči. Iz izmerkov preizkusov lahko ocenimo s Studentovo porazdelitvijo interval zaupanja in hkrati ponovljivost preizkusa. Če med preizkusom ne bi bilo drugih vplivnih veličin razen naštetih, bi lahko trdili, da je interval P , podoben spremenjanju vrednosti vulkanizacijskih lastnosti zmesi P_{mat} . Preglednica 3 prikazuje vrednost teh izračunov.

The systematic error of measurement of temperature always causes the same amount of error of measurement of ET values; the random error of measurement is annulled if integrated long enough. On the basis of test measurements the interval of confidence and the repeatability of experiments can be estimated by the Student's distribution. If there were no other influential values as those defined, it could be claimed that the interval P , resembles changes of the vulcanization properties of a compound P_{mat} . The values of these calculations are shown in Table 3.

Preglednica 3: Raztros vrednosti točke poroznosti

Table 3: Value scattering of point of porosity

	zagozda, wedge	kocka, cube
$P_1 \text{ min}$	0,99	0,78
število vzorčnih enot - N number of sample units - N	41	36

Preglednica 4: Izračun ponovljivosti N-te stopnje

Table 4: Calculation of repeatability of N-th degree

	zagozda, wedge min	kocka, cube min
B_{EM}	0,2	0,2
$t S$	0,99	0,74
$(t S)_{\text{vzorca, spec}} = t S / (N)^{0.5}$	0,15	0,12
U_{EM}^N	1,01	0,76
$U_{EM \text{ vzorca, spec}}^N$	0,25	0,23

Določitev intervala zaupanja s 95-odstotno verjetnostjo za nahajanje povprečje rezultatov vzorčne skupine pri ponovni določitvi točke poroznosti z enakim številom vzorčnih enot, nespremenjenim kalupom in nespremenjenim spremenjanjem vrednosti vulkanizacijskih lastnosti zmesi P_{mat} prikazuje preglednica 4 [3].

Determination of the interval of confidence with 95 % of probability for the occurrence of average results of a sample group at repeated determination of the point of porosity by the same number of sample units, unchanged mould and the unaltered changes of the vulcanization property values of a compound P_{mat} is shown in the table 4 [3].

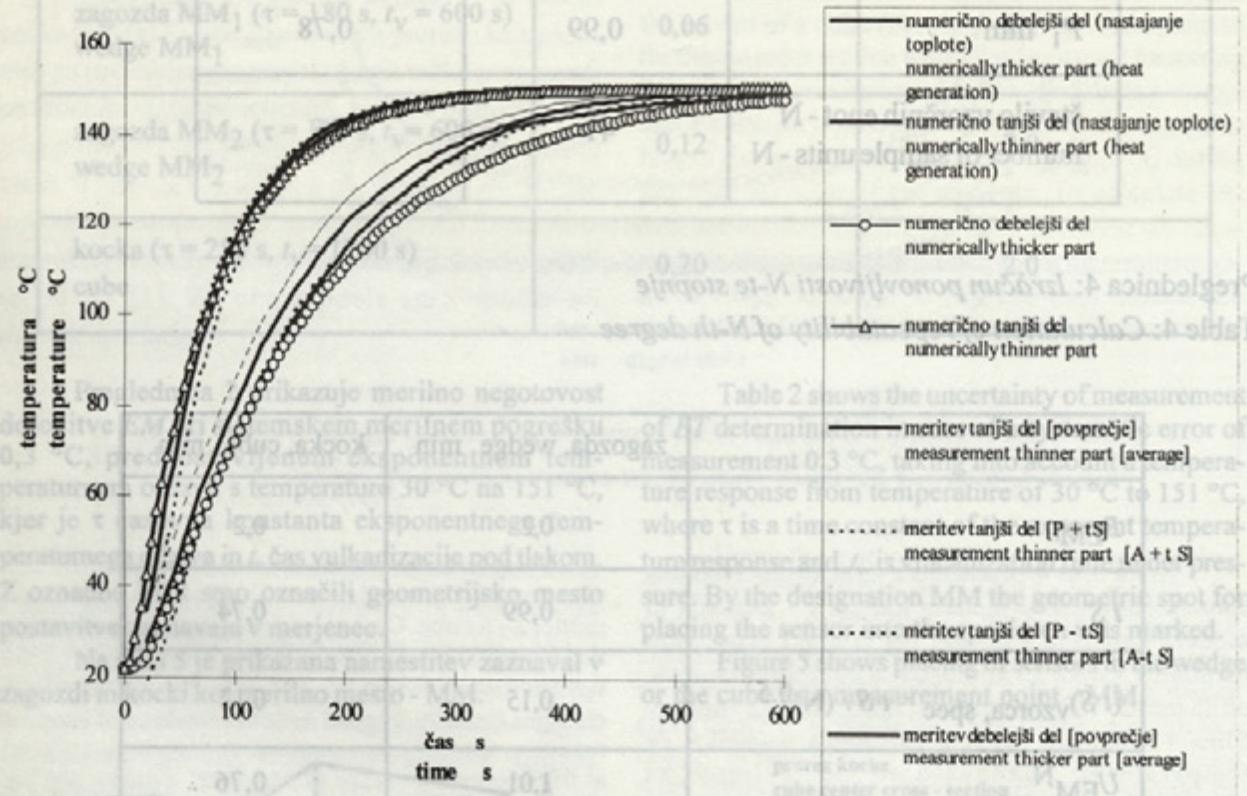
7 PRIMERJAVA TEORETIČNIH IN IZMERJENIH VREDNOSTI

Glede na dosedanje izkušnje smo pri vulkanizaciji uporabljali metodo določitve mesta točke poroznosti glede na izmerjene reološke vrednosti. Praktični preizkusi so pokazali, da se za večino zmesi za avtomobilsko pnevmatiko reološki izmerki spremenijo skladno in z izmerki za točko poroznosti.

To dejstvo nas je privedlo do sklepa:

$$\text{Točka poroznosti} \leq T_{\text{rheometer}} + C \quad (4)$$

Glede na lege temperaturnih zaznaval v zagozdi in kocki med preizkusom točke poroznosti merjencev lahko primerjamo izračunan temperaturni odziv na sredini merjencev z izmerjenimi (sl. 5)



Sl. 6. Primerjava teoretičnih in izmerjenih vrednosti temperatur zagozde
Fig. 6. Comparison of theoretical and measured temperature values for the wedge

Slika 6 prikazuje primerjavo teoretičnih in izmerjenih temperatur v zagozdi za namestitev zaznaval MM₁ in MM₂. Prikazan je odgovor prehoda za gumeni zmes brez nastajanja toplotne in z nastanjem toplotne. Izmerki so prikazani s srednjivo vrednostjo in intervalom tS po Studentovi porazdelitvi. Pri preizkusu je bilo treba merjenc vstaviti v kalup in šele kasneje smo lahko kalup vstavili v stiskalnico.

7 COMPARISON OF THEORETICAL AND MEASURED VALUES

With reference to our experience up to now, the spot of the point of porosity was determined on the basis of measured rheologic values. Practical experiments showed that in the majority of compounds for automotive tyres the rheologic measurements and the measurements of the point of porosity change in agreement with each other.

This fact led us to the following conclusion:

$$\text{Point of porosity} \leq T_{\text{rheometer}} + C \quad (4)$$

With reference to the position of temperature sensors in the wedge or the cube during the test of the point of porosity of specimens the calculated temperature response in the middle of specimens can be compared to the measured ones (Fig. 5).

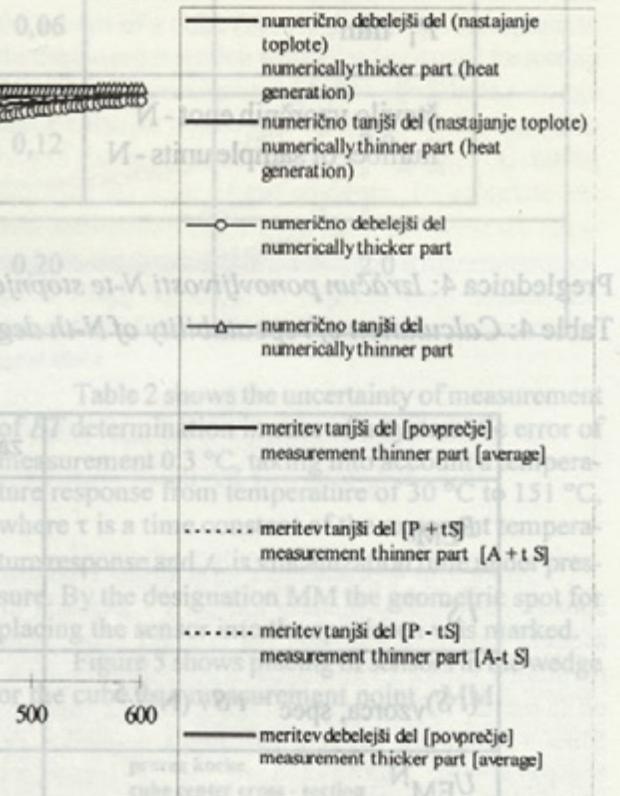


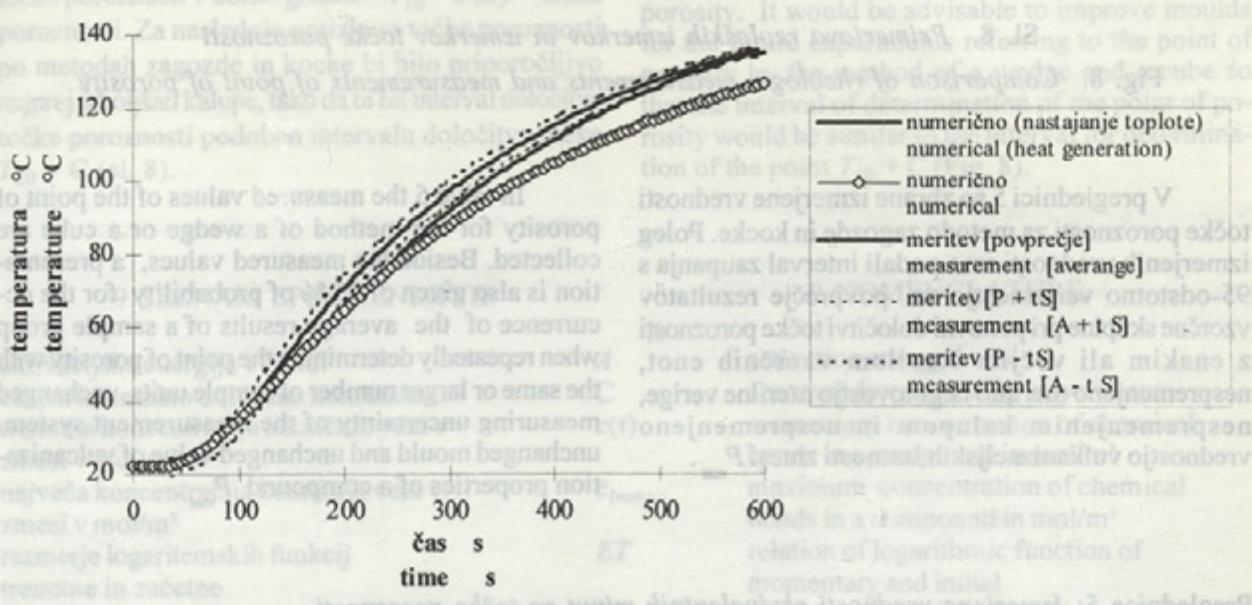
Figure 6 shows the comparison of theoretical and measured temperature in the wedge for sensor placing MM₁ and MM₂. The temperature response of a rubber compound without heat generation and with heat generation is presented. The measurements are presented with the mean value and the interval tS according to the Student's distribution. The specimen had first to be inserted into the mould, and only after that could the mould be inserted into the press.

Posledica tega je bil časovni zadržek, ki pomeni zaostanek spremeljanja spremjanja temperatur z merilnim instrumentom. Časovni zadržek smo med preizkusi z zagozdo izmerili in je znašal 21 ± 5 sekund.

Slika 7 prikazuje podobno primerjavo odgovora prehoda za gumeno zmes v obliki kocke. Tudi v tem primeru smo naredili izračun za zmes brez nastajanja toplote in za zmes z nastajanjem toplote. Izmerki so prikazani s srednjo vrednostjo in intervalom tS po Studentovi porazdelitvi. Izmerjen časovni zaostanek med preizkusi je znašal 34 ± 7 sekund. V obeh primerih opazimo relativno dobro ujemanje teoretičnega in izmerjenega odgovora prehoda za zmes z upoštevanjem enakomerne in homogenega nastajanja toplote med preizkusom.

The consequence was a time delay, which means the delay of temperature change monitoring by means of a measurement device. Time delay during experiments with the wedge was measured and amounted to 21 ± 5 second.

Figure 7 shows similar comparison of the temperature response for rubber compounds in the cube. In this case as well, we made a calculation for a compound without heat generation and for a compound with heat generation. The measurements are presented with a mean value and the interval tS according to the Student's distribution. The measured time delay during experiments amounted to 347 seconds. In both cases a relatively good conformity is observed between theoretical and measured temperature response for a compound, taking into consideration the uniform and homogeneous heat generation during the experiment.

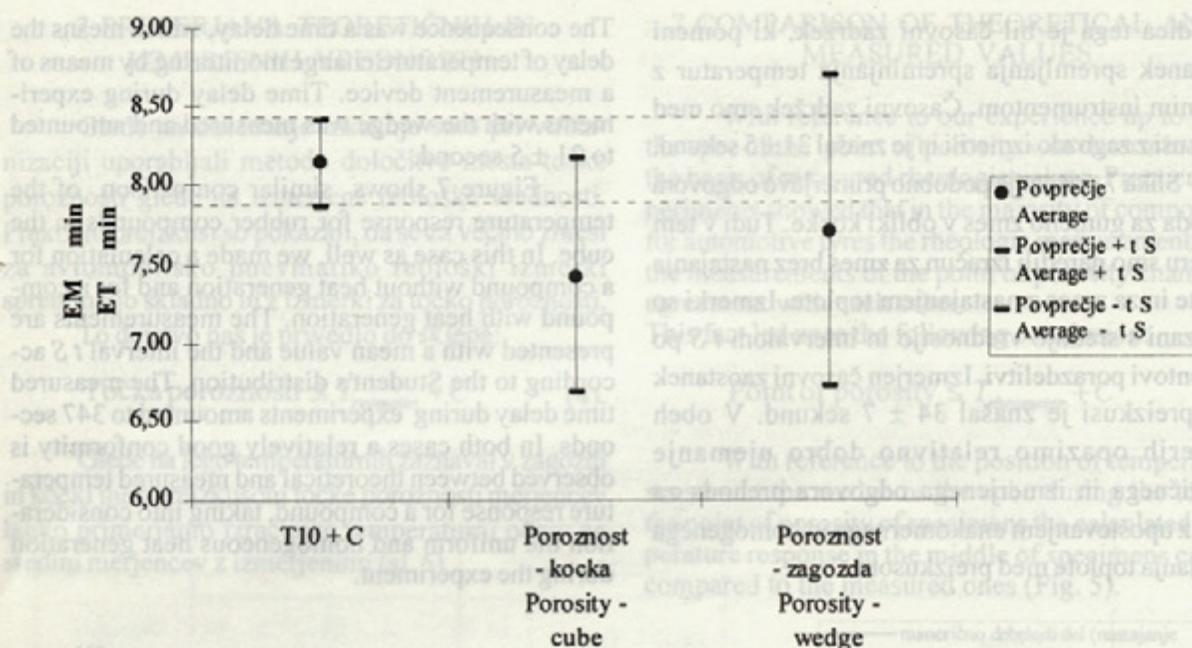


Sl. 7. Primerjava teoretičnih in izmerjenih vrednosti temperatur kocke

Fig. 7. Comparison of theoretical and measured temperature values for the cube

Slika 8 prikazuje primerjavo srednje vrednosti in intervala tS za izmerjeno točko poroznosti po metodi zagozde in kocke z reološko fiksno točko $T_{10} + C$. Vrednost konstante C je pri tem vnaprej določena. Slike opazimo, da so intervali raztrosov izmerkov $T_{10} + C$, točke poroznosti z metodo zagozde in kocke različni. V veliki meri je to zaradi konstrukcije kalupov in vira tlaka (oljna črpalka), ki niso zagotavljali ves čas trajanja preizkusa konstantnega tlaka.

Figure 8 shows the comparison of the mean value and the interval tS for a measured point of porosity according to the method of a wedge and a cube with a rheologically fixed point $T_{10} + C$. The value of the constant C is determined in advance. The Figure shows that intervals of the scattering of measurements of $T_{10} + C$ of the point of porosity by the method of a wedge or a cube are different. To a great extent this is due to the mould design and pressure source (oil pump), which could not ensure a constant pressure during the experiment.



Sl. 8. Primerjava reoloških izmerkov in izmerkov točke poroznosti

Fig. 8. Comparison of rheologic measurements and measurements of point of porosity

V preglednici 5 so zbrane izmerjene vrednosti točke poroznosti za metodo zagozde in kocke. Poleg izmerjenih vrednosti smo podali interval zaupanja s 95-odstotno verjetnostjo za povprečje rezultatov vzorčne skupine pri ponovni določitvi točke poroznosti z enakim ali večjim številom vzorčnih enot, nespremenjeno merilno negotovostjo merilne verige, nespremenjenim kalupom in nespremenjeno vrednostjo vulkanizacijskih lastnosti zmesi P_{mat} .

In table 5 the measured values of the point of porosity for the method of a wedge or a cube are collected. Beside the measured values, a presentation is also given of 95 % of probability for the occurrence of the average results of a sample group when repeatedly determining the point of porosity with the same or larger number of sample units, unchanged measuring uncertainty of the measurement system, unchanged mould and unchanged value of vulcanization properties of a compound P_{mat} .

Preglednica 5: Izmerjene vrednosti ekvivalentnih minut za točko poroznosti

Table 5: Measured values of equivalent minutes for the point of porosity

vrsta meritve type of measurement	zagozda, wedge (N = 41) min	kocka, cube (N = 36) min
posamezna meritev single measurement	$7,72 \pm 1,01$	$7,43 \pm 0,76$
vzorčna meritev sample measurement	$7,72 \pm 0,25$ (N ≥ 41)	$7,43 \pm 0,23$ (N ≥ 36)

8 SKLEP

8 CONCLUSION

Točka poroznosti pomeni pomembno informacijo o optimalnem času vulkanizacije obravnavane zmesi. Kakovostno bodo surovci avtomobilskih pnevmatik vulkanizirani takrat, ko bodo vsi sestavni deli plašča optimalno vulkanizirani. Gospodarnost nas v tem primeru sili k čim krajšim časom vulkanizacije surovcev. Če želimo povečati gospodarnost, moramo poznati vulkanizacijske lastnosti zmesi, temperaturno in tlačno stanje v surovcu in v okolini ogrevanega surovca avtomobilskega plašča [9].

Povezava med točko poroznosti in reološkimi lastnostmi zmesi bo v prihodnje koristna, ker se je nadzor zmesi na reometru že uveljavil. Tako bi dobljene informacije iz reometra lahko uporabljali tudi za določitev točke poroznosti. Najbolje bi bilo v prihodnosti dobiti eksperimentalno določeno povezavo med reološkimi izmerki in izmerjenimi vrednostmi točke poroznosti v obliki grafa $x = T_{10} + C$ in $y = \text{točka poroznosti}$. Za naslednje preizkuse točke poroznosti po metodah zagozde in kocke bi bilo priporočljivo najprej izboljšati kalupe, tako da bi bil interval določitve točke poroznosti podoben intervalu določitve točke $T_{10} + C$ (sl. 8).

The point of porosity presents important information on the optimum vulcanization time for the compound dealt with. The vulcanization of green tyres will be of quality when the components of a tyre are optimally vulcanized. Economic efficiency demands that the vulcanization times for green tyres be as low as possible. Should the economic efficiency be increased, one has to be familiar with the vulcanization properties of a compound, temperature and pressure conditions in a green tyre and in the surrounding of a heated green tyre as well [9].

The connection between the point of porosity and the rheologic properties of a compound should be of use in the future, since the inspection of compounds by rheometers is already being well brought into effect. The most desired improvement for the future would be to complete an experimentally determined connection between rheologic measurements and the measured values of the point of porosity in the form of a graph $x = T_{10} + C$ and $y = \text{point of porosity}$. It would be advisable to improve moulds for the future experiments referring to the point of porosity by the method of a wedge and a cube so that the interval of determination of the point of porosity would be similar to the interval for determination of the point $T_{10} + C$ (Fig. 8).

9 SEZNAM SPREMENLJIVK

aktivacijska energija v J/mol	A
eksperimentalno določena konstanta	C
trenutna koncentracija kemičnih vezi v zmesi v mol/m ³	$c(t)$
največja koncentracija kemičnih vezi v zmesi v mol/m ³	$c_{(\text{maks.})}$
razmerje logaritemskih funkcij trenutne in začetne koncentracije kemičnih vezi v zmesi za kemično reakcijo	ET
prvega reda v s	
konstanta časovne pretvorbe	K
hitrost kemične reakcije v 1/s	k
splošna plinska konstanta (8314,14 J/(kmol K))	R
izmerjena ali določena absolutna temperatura v K	T
fiksno izmerjena točka na reometru	T_{reometer}
čas v s	t
vulkanizacijski učinek	VE
razmerje trenutne in največje koncentracije v zmesi	x
referenčna temperatura v °C	θ_0
časovna konstanta v s	τ

9 NOMENCLATURE

activation energy J/mol	A
constant determined by experiment	C
momentary concentration of chemical bonds in a compound in mol/m ³	$c(t)$
maximum concentration of chemical bonds in a compound in mol/m ³	$c_{(\text{maks.})}$
relation of logarithmic function of momentary and initial	ET
concentration of chemical bonds in a compound for chemical reaction of the first order in s	
time transformation constant	K
speed of chemical reaction in 1/s	k
general gas constant (8314.14 J/(kmol K))	R
measured or determined absolute temperature in K	T
fixed measured point on rheometer	T_{reometer}
time in s	t
vulcanization effect	VE
relation between the momentary and the maximum concentration of chemical bonds in a compound	x
reference temperature in °C	θ_0
time constant in s	τ

8 CONCLUSION

10 LITERATURA
10 REFERENCES

8 SKLJEV

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Naslova avtorjev: Uroš Ilić, dipl. inž.
SAVA d.d.

Tovarna avtopnevmatike - QMT
Škojeloška cesta 6
4000 Kranj

doc. dr. Ivan Bajšić, dipl. inž.
Fakulteta za strojništvo
Univerze v Ljubljani
Aškerčeva 6
1000 Ljubljana

Authors' Addresses: Uroš Ilić, Dipl. Ing.
SAVA Ltd
Car tyre factory - QMT
Škojeloška cesta 6
4000 Kranj, Slovenia

Doc. Dr. Ivan Bajšić, Dipl. Ing.
Faculty of Mechanical Engineering
University of Ljubljana
Aškerčeva 6
1000 Ljubljana, Slovenia

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