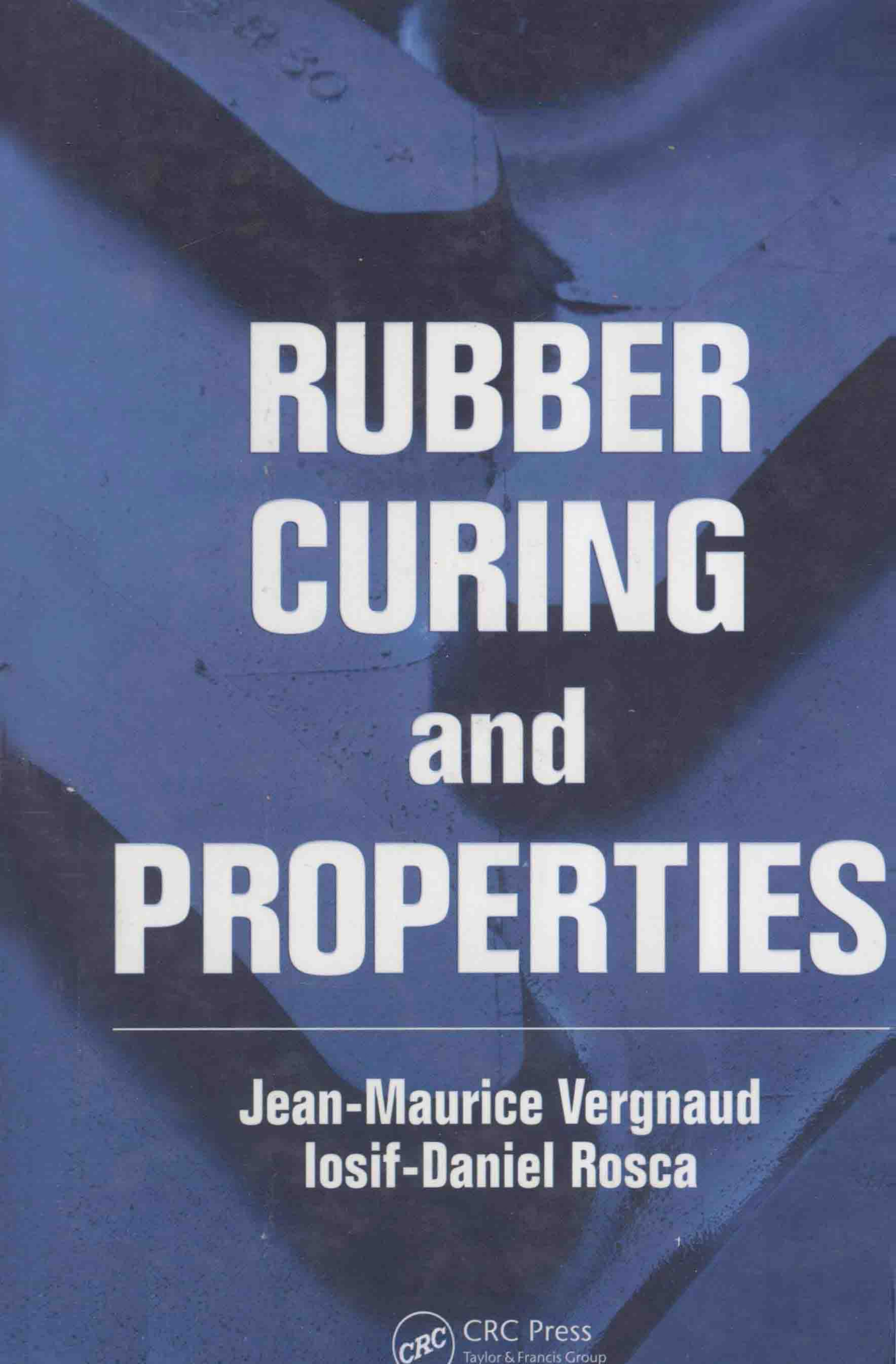

RUBBER CURING and PROPERTIES

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Preface

Rubbers are widely used in various applications, from tires to flexible tubings or absorbing systems, to mention just a few applications. They are favored when, in sharp contrast to other engineering materials, their relatively stronger attributes are needed and, at the same time, their highly deformable characteristics are desirable. Exhibiting almost complete recovery, they are virtually incompressible with a bulk modulus some thousand times greater than its shear or than Young's modulus. Moreover, rubbers are to some large extent impermeable to liquids and, especially, to gases. Both these qualities are of considerable value for tires in their utility on cars, planes, or bicycles. Thus, to sum up the importance of rubber in our life, it is virtually irreplaceable. It was said in 1941, when the United States decided to get involved in the Second World War, that no war could be started when no rubber is available in a country.

But the physical properties of a rubber material are not only innate; they largely depend on the state of cure of the final compound, as well as on the nature of the initial fresh rubber selected for the cure, this uncured rubber being either natural or synthetic. Following the process of cure, the compound, made of uncured rubber and of curing agents as well as of additives, is heated in a mold up to a temperature at which the reaction starts, the shape of the final material being given by the mold. During the cure, an irreversible reaction takes place, leading to a three-dimensional molecular network, and the plastic material is converted into an elastic one.

Thus, good knowledge of the process of cure is of high concern, for three reasons at least: the quality of the final product depends on the value of the state of cure as well as of its homogeneity through the material; moreover, it cannot be recycled if it is badly cured; and, for economical reasons, in addition, it is necessary to reduce the cure–time cycle.

Coming back to the process of cure, it consists essentially of two stages—that is, the heat transfer by conduction through the rubber mass as well as at the mold–rubber interface, and the cure reaction which starts at a temperature around 120–150°C, depending on the nature of the material. When the mold temperature is too low, the reaction is not achieved properly, and the final material, generally visco-elastic, has little interest for industrial application. Conversely, when the temperature is too high, the final material is burnt and breaking, without any quality of elasticity. Moreover, there is a narrow temperature window through which the reaction should be conducted. Thus, considerable importance needs to be given to obtaining a good understanding not only of the thermal properties of the rubber material during the heating stage and the cure process in the mold, but also on the values of the parameters necessary to express the kinetics of the cure reaction. By simplifying the principle of the cure reaction, which is essentially highly complex, and taking it as an nth order reaction, only four kinetic parameters should be considered: the enthalpy of cure, which represents the heat evolved during the whole reaction; the two terms that enable the measurement of the temperature sensitivity of the reaction, i.e., the energy of activation and the rate constant that counterbalances the effect of the energy of reaction; and the amount of rubber remaining uncured, which is to the nth power, n being the order given to the overall reaction. And thus, in time, various techniques have been developed and used so as to determine the kinetics of the cure reaction from which are calculated the main kinetic parameters.

The importance given to the kinetics of cure is so great that various techniques have been tested or even created for determining the parameters of the kinetics of cure, the cure being considered on the whole as conforming to the Arrhenius's expression.

The first was calorimetry, conducted either under isothermal conditions or in a scanning mode with a constant heating rate. However, though this technique may be very well adapted to the cure of thermosetting resins, which develop a large enthalpy, it is not the perfect one in the present case, because of the rather low value of the cure enthalpy of rubbers, which does not exceed 8 Joules/gram rubber per 1% sulfur. Isothermal calorimetry has been used by assuming that the rate of cure varies with temperature according to an Arrhenius equation. The differential scanning calorimetry (DSC) technique has been employed for defining the temperature at which the reaction starts. The cure enthalpy has been obtained from DSC experiments. A question arose in the mid-eighties as to which could be the best calorimetry technique, the isothermal or the DSC. And finally in-depth studies on the process of heat transfer through the sample showed that in isothermal calorimetry, the operation is not as simple as it first looks; the sample initially at room temperature is dropped into the calorimeter, which is kept at the selected temperature, and the strong heating stage may hide the first part of the reaction, considerably reinforced by the fact that a temperature window of about 30 K is found over which meaningful data can be obtained. Finally, it has been proved that calorimetry in scanning mode is the best technique for evaluating not only the cure enthalpy, for thermosetting resins at least, but also for determining the kinetics of heat evolved from the overall cure reaction.

Another technique, interesting but highly time-consuming, was based on the measurement of the swelling of the rubber samples taken at various stages during the cure. In the late seventies, this method was used not exactly for measuring the kinetics of the cure reaction but especially for evaluating the state of cure for a given rubber-curing agent couple. Thin rubber sheets (0.5 mm) were heated isothermally within a range of time and temperature, and the state of cure was evaluated by measuring swelling in toluene of these final samples; afterward, using the data obtained, the degree of cure profiles in thicker blocks (25 mm) were calculated and compared with the profiles experimentally determined.

Other studies have been carried out by considering the heat transfer by conduction through the rubber, as well as the heat generated by the overall cure reaction. The state of cure at any time *t* is thus defined as the heat evolved up to time *t* as a fraction of the total heat evolved from the cure reaction. In a particular method, the state of cure was calculated from the temperature history at any place in the rubber by introducing a rate of reference at 149°C and a temperature coefficient of cure, assuming that the rate of cure increases by a factor of 1.85/10°C. In another study, the profiles of temperature developed through the rubber were calculated assuming that the rate of cure doubles for each 10°C increase in temperature around the temperature reference of 150°C. This reference temperature method avoids the use of the order of the reaction, but necessitates a full study of the material at this reference temperature. As the problem of heat transfer by conduction with internal heat generated by the cure reaction cannot be mathematically resolved, numerical models have been built by taking all the known facts into account, for various shapes of the material, either in the cylindrical sample in the calorimeter or more simply in the sheet located in the slabs of the heated mold.

Other methods widely used for the cure of rubbers consist of heating the sample and monitoring the viscosity or torque of the rubber during the cure. The Money viscosimeter, the Wallace–Shawbury curometer, the oscillating disc rheometer (ODR), and the moving die rheometer (MDR) have been developed and marketed, the MDR being introduced in 1985.

All these setups work under isothermal conditions. In the MDR, a thin sheet (around 2 mm) is placed between the two dies kept at the desired temperature; the lower disc oscillates and a reaction torque/pressure transducer is positioned above the upper die. It has been found that the MDR gives shorter times of cure than the ODR because of better heat transfer and higher torque values owing to the die design. The MDR is run at three temperatures to allow evaluation of the kinetic parameters of the cure reaction. Thus, the activation energy and the preexponential factor can be calculated from the fractional modulus time values obtained with this apparatus. The modulus value is assumed to vary with time following first-order kinetics, and the rate constant varies with temperature according to the Arrhenius equation.

The process of curing rubber taking place in the MDR is similar to that in a mold: heat transfer by conduction through the rubber with a coefficient of heat transfer at the die–rubber interface, followed by the cure reaction. Thus, with the MDR run under isothermal conditions, when the sample initially at room temperature is introduced between the heated dies, considerable heat transfer occurs through the rubber with a corresponding decrease in temperature at the die surface. As a result, steep gradients of temperature develop through the thickness of the rubber sample. The cure reaction starts at a given temperature and gradients of state of cure are expanded with a higher value on the surface in contact with the dies. After a time, the profiles of the state of cure become more and more uniform.

Then, three parameters become of great interest, regardless of the nature of the rubber and curing agent: the temperature of the dies, the thickness of the sample, and the quality of the contact between the rubber and the dies. It is not easy to place correctly the rubber sample between the dies when they are heated. And, moreover, another drawback brought by the isothermal conditions necessitates the right selection of three temperatures within a narrow temperature window. This is the reason why attempts have been made recently to upgrade this MDR technique by using it in scanning mode in various ways. Thus, instead of having to make three measurements with different samples at the selected temperatures, only one experiment is necessary. First, the scanning mode with a constant rate has to be considered from the beginning to the end of the process. In order to improve this process and to reduce the time of the experiment, a change in the rate of heating has been introduced, with a high rate at the beginning, followed by a lower rate as soon as the cure reaction takes place. Moreover, the effect of parameters of interest has been deeply studied, such as the heating rate and the quality of the contact between the rubber and the die. Finally, it has been found that the linear increase of temperature with time is perhaps not the best way of heating the apparatus, as a square root of time–temperature programming was proved to be shorter in time for the MDR used for the cure of rubber.

Another problem should be considered in detail with the process of curing the rubbers in the mold; this occurs when the cure reaction takes place, and is associated with the heating stage.

Thus, from the measurements providing the values of the kinetic parameters of the cure reaction, it is possible to evaluate the progress in the cure of a piece of rubber by using also the thermal parameters of the rubber and of the mold. In spite of the low value of the heat generated by the cure reaction, the profiles of temperature and of the state of cure developed through the sample at various times are obtained either by experiments or by calculation. Calculation is made by considering the heat transfer by conduction not only through the rubber but also through the mold, as the mathematical treatment is not possible in this case; numerical models, taking all known facts into account, have been built and successfully tested. Different topics concerned with the cure of rubbers and their properties, such as the process of cure and the methods of evaluating it through modeling, the correlation between the state of cure of the rubbers, and either their mechanical properties or their resistance to liquids, have thus been established.

Testing of rubber materials involves exposure to various types of environmental factors. One of the most important problems for rubbers is their resistance to liquids. The tests in which rubbers are in contact with liquids are often called "swelling tests," because of the resulting change in volume of the test piece, or also "oil aging tests" because mineral oils are the liquids most specified. These tests generally consist of measuring the total uptake of toluene by a rubber after immersion in the liquid. Another way was explored by studying the process of absorption or desorption of the liquid previously absorbed, which are both controlled by diffusion through the rubber with a change in dimensions leading to typical boundary conditions. As the problem cannot be resolved by mathematical treatment, various numerical models have been built and tested, so as to take into account not only the diffusion with a concentration-dependent diffusivity and the change in dimensions but also the anisotropic swelling. The way of evaluating the concentration-dependency of the diffusivity, already successfully traced by using other polymers, has been used for these problems involving rubber.

Because of their typical properties in terms of mechanics, measuring the mechanical properties of rubber is of great concern. These are determined not only under static conditions but also under dynamic conditions, with the in-phase and out-of-phase modulus.

The main objectives of this book are varied. The first consists of giving, in Chapter 1, a bird's eye view of the history of the cure process by recalling a few previous experiments and calculations of interest, which should be considered as decisive hallmarks in the developing of rubber curing processes.

In the second chapter, all the problems set by the process of heat transfer are considered, with convection at the solid–fluid interface, and with conduction through a solid, which can be the rubber or the mold. The situation of heated rubber after the extraction out of the mold requires an application of the heat process connecting the convection and the conduction.

In the third chapter, the methods used for evaluating the kinetics of the cure of rubbers are described and studied on the basis of either the heat evolved from the cure reaction (calorimetry) or the change in the mechanical properties during the cure (rheometers). Theoretical studies are made so as to improve either the isothermal MDR, or even the MDR in scanning mode, by considering different temperature–time relationships.

In Chapter 4, applying the information given in the two previous chapters is discussed in detail for the cure of rubber sheets in molds. Monodirectional heat transfer is thus considered, but the case of three-directional heating systems is also examined. The effect of various parameters such as the values of the kinetic data (rate constant, energy of activation, enthalpy of reaction, and order of the overall reaction); the thermal transfer data of the rubber; the characteristics of the mold; and finally the relation between the rubber and the mold are included. The important area of multilayer rubbers of various types has also been considered by combining the effects of diffusion of the active agents between these layers during the cure with the heat transfer and then the cure of the system. Thus, it is shown that this diffusion enables a final rubber system for which the properties vary continuously through their thickness, leading to high adhesion between these layers. The postcure of the already-cured rubbers that may take place when they are extracted out of the mold is also examined.

In Chapter 5 the principle of the injection molding principle is described, with its obvious advantage in reducing the time of the cure; the temperature at which the rubber can be injected without detriment to the mold filling is also evaluated. The important problems set up by the plasticity and by the scorch—that is, the onset of vulcanization—are probed in depth. If the isothermal MDR technique is able to give a rough idea of the scorch time, it is shown that the MDR run in scanning mode—that is, the apparatus commercially called the rubber process analyzer (RPA)—is capable of providing two characteristics of the scorch, the time and temperature.

An attempt is made in Chapter 6 to relate the mechanical property of the rubber under dynamic conditions to the state of cure. The mechanical properties of the unvulcanized rubber are also evaluated, with plasticity versus temperature and the scorch. The mechanical properties of the vulcanized rubber are then considered, in static and dynamic modes.

In Chapter 7, in-depth studies are made on the resistance of rubbers to liquids, which is expressed by the amount of the liquid absorbed or, much better, by the kinetics of absorption. The process of liquid absorption in the rubber material, as well as of that of desorption of the liquid previously absorbed, are studied. These processes are driven by transient diffusion, which is examined in terms of rubber. As rubber may absorb a large quantity of liquid, a swelling takes place; thus, the diffusivity is not only concentration-dependent, but also the boundary is moving with the amount of the liquid absorbed. On the other hand, it will be seen that the processes of diffusion and cure can occur simultaneously, because a diffusion of the active agent is proved to take place through the interface between two rubber layers with different percentages of sulfur when they are cured together.

Chapter 8 is devoted to the on-going problems of recycling scrap rubber tire, in spite of the fact that this subject is somewhat beyond the scope of this book. Various solutions are regarded in succession, including burning, using pyrolysis in order to get some residues of interest, and using solvent as an agent of devulcanization. Finally, by considering scrap rubbers as new raw materials, the method based on vulcanizing the compound obtained after addition of curing agents to the scrap rubber, either in its pure state or in addition to fresh rubber, is especially studied.

Our book presents its main findings in terms of equations and figures. In all cases, the theoretical treatment is offered in a didactic manner, so that readers who are not fully familiar with the terms can, nevertheless, easily understand the developments in this field. The assumptions for which the calculations are made, and the solutions obtained, are clearly presented. It is true that the problems of heat transfer by conduction, as well as those of diffusion of liquid through a rubber, are not easy to understand. This is the reason why the solutions of the differential equations with partial derivatives that express these transfers are explained in detail. On the other hand, in order to facilitate the reader's understanding of the results, the figures are drawn by using dimensionless numbers as coordinates as often as possible; as a result, master curves are obtained that are of value in various applications.

Thus, by introducing the typical values of a problem, readers can obtain the result of the actual problem put before them.

The data published by various authors are given, so as to help readers in making their own calculations. They include the values that deal with heat transfer and the kinetics of the cure reaction, and cover the diffusion of liquids through rubber. In each case, references are given.

Finally, it should be added that various books of interest have already been published on rubber in domains other than the one considered in the present book: the process of cure and properties of the vulcanizates as a function of the state of cure. They are cited as much as possible. Among them, *Physical Testing of Rubbers* [1] is worth noting, and various notations are drawn from this book, especially in Chapters 2, 3, 4, 6, and 7. Let us remark that at the time the fourth edition of Brown's book had just been launched on the market; the objective of the present book on the cure of rubbers, however, being different from that of Roger Brown's, this first edition only has been considered. On the other hand, *The Analysis of Rubber and Rubber-like Materials* [2] is of interest as far as the chemistry of rubbers is concerned. Three other books are cited, as they contain at least one chapter devoted either to the cure of rubber [3] or to the stage of absorption of liquid [4], and to the subsequent stage of drying rubber containing a liquid [5]. One of the most specialized books on carbon black is also cited in Chapter 8, which is concerned with reclaiming scrap rubber [6]. But in all cases, the theory of the cure process has been developed and updated, and the results especially applied to rubber materials in the present book.

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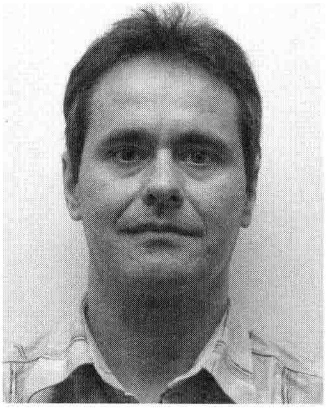
Jean-Maurice Vergnaud is a professor at the University of Saint-Etienne, France, retired from teaching but not from research. He has earned several awards, either in industry or at university: the Prize of the French Chemical Industry (new methods in gas chromatography) in 1966; Silver Medal from the French Academy of Sciences (molecular sieves) in 1976; the George Stafford Whitby Award from the American Chemical Society, Rubber division in 1998; and the Gold Medal from the French Society for encouraging progress in 2007. He is the author of 450 papers and 300 communications, 30 plenary lectures, and has been speaker at 10 sessions of the prestigious Gordon Research conferences. He is the author of eight books published by international publishing companies, and belongs to the editorial boards of five international journals.



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Contents

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7