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BULGING (INFLATION) OF NATURAL RUBBER COMPOUNDS DURING THEIR FORMING

by R.Chasset, J.C.Touraine, H. de Livonniere

The dimensional stability of the rubber mixtures sometimes grows from one to other during their transformation. The elastic, pick-up of mixies (compounds), the characteristic which can be measured by a plastorecovermeter could serve as criterion so as to detect the variability of bulgings observed after transformation.

INTRODUCTION

There exists no single test to characterize the operation of elastomeres and compounds (mixies), the word "operation" in fact covers very different properties put together.

In reality, the operation can only be defined from different operations which it carries:
-degradability, effectiveness of mastication to obtain the required consistancy;
-the behaviour of charges in mixing;
-extrudability
-dimensional stability during forming operations;
-injectability;
-Vulcanizing (curing)
-etc...

The problems of dimensional stability of compounds (mixtures) during operations of forming have specially attracted the attention of the authors. It is unanimously recognized that this stability is directly connected to the elastic pick-up of compounds (mixtures) consecutive to the deformations which they undergo in the extruding machines or on calandering machines(for example). Also, in the first approach, has an instrument been developed which can accurately measure the elastic pick-up of gums and mixtures: it is the plastorecover

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meter (1). It is a modern version of williams (2) and DEFO (3) and plastometer, designed to ensure especially the application and the releasing of the charge (load) in a shortentime possible, and in a reproducible manner, so as it can reach the response time of less than a second. An improvement of the DEFO has been recommended by Koopmann and Kramer (4).

THE MEASUREMENT OF ELASTIC PICK-UP

Description of elastic pick-up

The test essentially consists of submitting a cylindrical test-specimen, placed between two parallel plates, to a compression load for a given time (creep period) then to remove the load and to continue increasing of height of the test-specimen (period of elastic pick-up).

Principle of test (fig.1)

The test specimen (1) is put up between two parallel plates; the lower plate (2) is made-up of an aluminium block rigidly fixed to the bottom of oven so as to ensure a good thermal conductivity, whereas the upper plate (3) has the form of disc of 45 mm of diameter. This disc is joined to a rod (4) vertically guided with the minimum of friction, with the plate-red assembly having a weight of 110 g. The compression load is exercised by a weight (5) resting on the plate (6) which is rigidly connected to a rod (7) centered on the vertical axis of the test specimen. A beam (8) which can pivot around the horizontal axis (0) with the help of ball bearings: one of the arms of the beam is articulated in A on the rod of load-holder plate and the other is connected at B to a high-power electromagnet (9). A device containing a screw (10) enables, on onehand, to lock the beam in "up" position and, on the other hand, to bring the rod (7) of the load-holder plate in contact with rod (4) before each test. The system of locking of beam can be retracted by the electro-magnet (II) by operating perpendicularly as in Fig. Finally, a displacement probe, which is not shown here, is fixed to the rod (4) and enables to know at each instant the height of the test-specimen close to 1/100 of mm.

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We operate as follow, for carrying out a test, At a given time, the electro-magnet (11) releases the load; after a time for creep "to", the electro-magnet (9) releases the strain almost instantly and we observe the elastic shrinkage. The contact between the test-specimen and the upper plate is ensured by a force of nearly 0.1 N difference between the weight of plate and of rod and the action of compensating spring.

Thermostatic controlled enclosure

The test-specimen is kept in centre of an enclosure having inner dimensions of 250 x 160 x 200 mm, with metallic walls on which the electrical resistances of 300 watts power, are fixed. A fan ensures a mixing of air to obtain an homogeneous temperature. A regulation maintains the temperature between 70 and 140°C at close to ± o.2C. The measurements, with the help of a thermo couple introduced with test-specimens, have showed that a heat conditioning time of 7 minutes enables to reach the nominal temperature at the core of the test-specimen close to one degree.

Automation of tests

The data processing portion is explained in fig 2. The automation of tests is made by a micro-computer which sometimes works in/output (control of electro-magnets), sometimes in input (data acquisition).

The data acquisition chain essentially contains the computer, a numerical analog inverter (digital voltmeter and the movement probe which supplies a signal proportional to instant height of the test-specimen. The values acquired at well determined time in creep as well as in elastic pick-up appear on a printer and are stored on a disc.

The plastorecovermeter may operate between 70 and 140°C with the loads between 2 and 15 daN. The duration of creep varies between 1 second and 10 minutes, whereas that of the elastic pick-up, it can reach hours if necessary.

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Preparation of test-specimes

Use of two types of cylindrical test-specimes of same diameter is possible; one is of 10 mm height, the other is of 16 mm. The first type corresponds with Williams specimen, whereas the second shows the same factor of form as of the DEFO specimen, but its dimensions are bigger. Presently, the test-specimen of 16 mm of height is used , because of its smaller factor of form enables to minimise the influence of the armatures (frame).

Two techniques of preparation of test-specimens are envisaged:
-moulding of each test-specimen at 100°C in a mould with pistons by controlling the quantity of material introduced in each enclosure; the drawing out from the mould takes place at ambiant temperature after cooling under pressure;
-moulding at 100°C of plates of 10 mm of thickness and cut-out of test-specimes with rotative part-holder.

The first method gives the perfectly cylindrical specimes and of constant volume; with the second, the specimes are less regular and their form depends on feeding of rotative part-holder and hence on the operator.

So as to render the rubber/shieldings reprodutible, we have bonded on lower and upper plates, a sheet of teflon of 1 mm thickness with the teflon being periodically cleaned with a solvant so as to remove any danger of contamination of surfaces in time.

Method of expressing the results

If we designate by "Ho", the initial height of the specimen, by H(t) the height during creep under a load P, by HI, the height at time tI of releasing of load and by H'(t) the height during the elastic "pick-up", it is possible to characterize:in fig3:

<u>THE CREEP</u> by the relative height of the test-specimen h(t)=H'(t)/Ho, the more the h(t) is small, more the "viscosity" of the material is lower and the creep is higher;
THE ELASTIC PICK-UP by:

. the relative height of test-specimen h(t) = H'(t)/Ho

. increase of height of test-specimen reported with the maximum deformation at the end of creep.

Rt = H't - Hl, Ho - Hi

R(t) shows the advantage of bringing out the elastic pick-up taking into account the crushing undergone by the specimen during creep.

Tests carried out

Preliminary study

Initially, to establish the possibilities of the equipment , a study of physical parameters (temperature, load, duration of creep) has been carried out on PB rubber (the rubber of type"polybag" matured 4 weeks) of GT 1 after homogenization according to specification NF T 43-005. Its Mooney's consistancy (ML I+4-100°C) is equal to 100.

Three specimens have been used for each test condition. The dispersion of results is relatively low, the coefficient of dispersion (quotient of standard deviation by average) is between 1 and 2% for the creep and 3 to 5% for the elastic pick-up.

The effect of five temperatures has been examined: 70,90,110,125 and 140°C as well as four loads: 2,5,10 and 15 daN. For each combination, two durations of creep have been selected: they have been chosen in function of temperature and level of load.

In a general manner, we can state that :

-for a same load , more the duration of application , the pick-up is lower;
-for a same duration of application of load, the pick-up is so much higher as the load is lesser;
-even at 140°C and for a higher load, the elastic pick-up can be near total if the duration of application is reduced.

The influence of physical parameters has been examined, but in less exhaustive manner, over a different natural rubber, a ISO 50 rubber of Mooney's consistancy 43 as well as on the compounds

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consisting of 50 parts of a carbon black (HAF N 330) prepared from PB rubber of GTI and of ISO 50. The same observations as [illegible] previously have been made.

Moreover, in homegeneous condition as in charged mixture, the elastic pick-up of rubber if GT 1 is clearly higher than that of ISO 50, regardless the experimental conditions used as illustrated by few tests represented in figs 4 and 5.

Following these tests, it has been decided to retain the following as the experimental conditions:

-125°C and a load of 10 daN applied during 20 seconds for the homogenized rubbers;

-110°C and a load of 10 daN applied during 10 seconds for the loaded compounds;

The elastic pick-up is measured after a duration equal to 20 times of that of application of load.

Application with study of different rubbers

The parameters retained are the following:
-clone : GTI and PR 107;
-DRC: initial and dilution at 15%;
-coagulation : by acid or natural (PB);
-CV treatment;
-drying temperature;
-storing of rubbers upto 18 months.

The different rubbers have been examined at homogenized conditions and in mixtures containing 50 parts of (HAF N 330)black. The whole of the results obtained is resumed in few figures.

The figures 6 and 7 show the relation between the elastic pick-up and the creep respectively for the homogenized gums and the mixtures with black: we establish that the gums or the mixtures having nearby creeps can have the very different elastic pick-ups.

Besides even for homogenized rubbers as well as for mixtures with black (fig 8 and 9) the creep is correctly correlated with Mooney's consistancy, show higher dispersion of expt.al points.

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Thus, the elastic pick-up of gums and mixtures with black, does not seem to be directly connected to their Mooney's consistancy. In these conditions, the results obtained have not seems as sufficiently interesting so that an important study, including especially the bulging at extruding die and bulging at calendering be undertaken.

BULGING OF MIXTURES (COMPOUNDS) afterTHEIR FORMING

Extrusion (bulging in drawingby draw-plate (die extruder)).

The equipment used is the extruder of Rheomex 104 laboratory (Haake material) with stuffer with roller equiped with a carpet type conveyor so as to ensure, at the output of the extruder an unreeling of reed as regular as possible and to avoid especially any intervention from the operator which is prejudicial to the reproducibility of the tests.

The screw has a diameter of 19 mm (3/4") and an L/D ratio equal to 10; the speed is variable from 0 to 100 RPM. The (die) draw-plate has a diameter of 4.76 mm (3/16") and is relatively short (L/DM ratio 3.8).

The tests are conducted conforming to the specification ASTM D 2 230 - Method B with a temperature of 75°C and a speed of 100 RPM. The apparent shear speed is nearly 190s-1.

The bulging at die is expressed by (D-Do)/Do. where "Do" designates diamter of the draw-plate (die) and D, the diameter (mean diameter) of reed extruded, determined by weighing of reeds, the given length (1 ± 0.001 m), cut after two hours of rest. The coefficient of dispersion of tests is between 1 and 3%.

Calandring (Bulging (Inflation) at calandring)

The tests are carried out on a Lescuyer Malaxer (mixer) of laboratory (diameter of cylinders 150 mm), used in calandering. (friction ratio 1/1 - speed 24 RPM). The volume of mixture is always the same (M380 cm^3), with the guides being off-set by 23.5 cm. The temperature of cylinders is of 70°C.

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The method of operation is as follows:
-the mixture is passed to fine (gap 0.2 mm) then introduced between cylinders seperated by 1.5 mm; after nearly 30 seconds, the sleeve is thus formed and we give the gap between cylinders at 2 mm;

-soon after we cut the sleeve and we collect the calendered sheet over a paper which is abundantly covered with talc;

-after nearly 3 hours of rest at ambiant temperature. we cutout with the hollow-punch from the sheet make 4 plates of 15 x 4 cm by avoiding the edges area;

-by weight, we deduce the mean thickness of the sheet. The bulging at calandring is expressed by (e-eo)/eo.

where eo = 2mm represents the seperation of cylinders during calandring . The dispersion coefficient of tests remains between 2 and 5%.

COMPARISON BETWEEN ELASTIC PICK-UP AND BULGING (INFLATION) OF MIXTURES.

Observation on the measurement of elastic pick-up.

A preliminary study has led to the modification to the method of operation used till now, for measuring the elastic pick-up. Instead of carrying out this one after a creep of a determined duration, the deformation of specimen is limited to a constant value (for example 50%) and maintained during a given time: the load is then removed and the elastic pick-up is measured as before . The limitation of the deformation is easily obtained by a shim of appropriate height. For the mixtures with black the duration of maintaining of deformation is of 5 seconds and the elastic pick-up determined is noted as R5s 50%.

Such a procedure gives at least two advantages:
-the experimental conditions corresponds better than those come across during extrusion or during calandring: during these operation the deformations implied to the mixtures are less dependant on rheological properties of the latter but are rrather directly connected to technical characteristics of equipments used;

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by measuring the elastic pick-up after a creep of a duration which is still the same, the deformation is necessarily in function of the "Viscosity" of the considered material; thus it is susceptible to considerably vary from one mixture to the other, which is no more the case, with the new procedure.

- for the mixtures with lower Mooney's consistancy, the height of specimen at the end of creep can relatively become less, it results in a substantial increase of areas of contact between the specimen and the frame, from where the frictions appear, the limitating factor to observe the elastic pick-up representative of properties of mixture which is studied.

The new method of operation however presents a certain disadvantage: the informations on the viscous components (creep) are no more counted. In fact, it has been previously shown that the creep is narrowly correlated with the Mooney's consistancy of mixtures, so well that its determination is not indispensable.

Preparation of mixtures

The mixtures necessary for carrying out the extrusion tests, of calandring and of elastic pick-up tests are carried out in a werner internal mixer of laboratory:

-volume of mixing chanmber : 1.8 litre
-normal filling coefficient: 0.55 to 0.65
-effective capacity : 1 to 1.15 litre
-pneumatic actuator (travel 50mm): pressure 6 bars.
-speed of blades : 43 and 31 RPM
-power allowed in operation:3.5 KW
-cooling is possible by circulation of water.

The time of rest of the mixtures between their manufacture and whole of tests are strictly controlled.

Experimental results

A study of several grades of natural rubbers in mixtures with three carbon blacks (HAF N 330 - FEF N 550 - SRF N 762),

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at the rate of 30,40 and 60 portions each, is started. Till now, only one smoked sheet and one SMR CV 50 have been used and examination of three carbon blacks has not been completed; nevertheless, it is possible as of now, to present some of the results obtained.

The Mooney's consistancy of the homogenous gum is of 84 and of 49 respectively for the smoked sheet and SMR CV 50 and all the têsts (including the mixtures) have been repeated at least once.

The figure 12 shows the existance of a close correlation between the bulging inflation of the mixtures determined after extrusion, on one hand, and calandring on the other, in case of SMR CV 50 containing different proportions of black, HAF or SRF. In fact the coefficient of correlation "r" is equal to 0.898 (for a probavility threshold of 1% r = 0.708). In addition, the variations of bulging inflation at calandering (0.5 to nearly I) are more staggared than those of bulgings at die (Extrusion die) (0.9 to I.I).

If we now consider the variations of Extrusion-Die bulgings (fig.13) and those of bulgings at calandering (fig 14) in function of elastic pick-up of same mixtures, we also oberve a close correlation. The tests are relative to smoked-sheet and to SMR CV 50 containing different contents of HAF black.

Finally it is interesting to consider the variations of Die (Extrusion) bulging and the elastic pick-up, in function of the Mooney's consistancy of mixtures. It is the object of figures 15 and 16, relating to the mixtures containing the HAF black, with base of smoked sheet and of SMR CV 50.

It is surprising to state the different behaviour of the smoked sheet and of SMR CV 50 vis-avis the Mooney's consistancy of mixtures for extrusion-die bulging as well as for elastic pick-up.

-The smoked sheet: There appeared no significant correlation between extrusion-die bulging or the elastic pick-up and the

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Mooney's consistancy (the coefficients of correlations r 0.70 and 0.75 corresponding to the thresholds of probability closer to 10%):-The SMR CV50 : on the other hand, the values of correlation coefficients (0.91 and 0.92, i.e. the probability of 1%) show that for this rubber, extrusion die bulging and elastic pick-up are in close ration with the Mooney's consistancy of mixtures.

At this condition of study, it is not possible to explain this difference in behaviour.

CONCLUSION:

Even though the results which are going to be presented still does not constitute sufficiently substantial document in our opinion, it brings out, the reflection items on the problem embarked upon in the frame work of this communication: the dimensional stability of mixtures during their forming.

An approach, in the form of a laboratory test, is proposed: the elastic pick-up of mixtures. This characteristic can it be used as standard to reveal the varialbility of bulgings obersved sometimes from one batch of rubber to the other?

We would very much like to know the opinions of the natural rubber producers and the manufacturers and to collect their suggestions so as to orient the future researched in useful manner.

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Rubbers of latex of GTI.
Rubbers of Latex of PR 107
Rubbers of Latex of GTI treated CV.

Fig.8. Correlation between the creep and the Mooney's consisancy for the homogenized rubbers.

Fig 9. Correlation between the creep and Mooney's consistancy for the mixtures containing 50 parts of HAF N 330 black.

Fig 10 Variations of elastic shrinkage in function of Mooney's consistancy for the homoenized rubbers.

Fig 11 Variations of elastic shrinkage in function of Mooney's consistancy for the mixtures containing 50 parts of HAF N 330 black.

Figs 8 to 11. Drying temperature, coagulation by acid natural CV treatment.

Fig 12 Correlation between the bulging and the calandering for a SMR CV 50 containing different proportions of HAF N 330 black or of SRF N 762 black.

Fig 13 Correlation between bulging and the elastic shrinkage of mixtures containing HAF N 330 black prepared from a smoked sheet and from a SMR CV 50.

Fig 14 Correlation between the bulging with calandering and the elastic shrinkage of mixtures containing the HAF N 330 black prepared from a smoked sheet and from a smr CV 50 black.

Fig 15.Variations of bulging at the in function of thise of the Mooney's consistancy of nmixtures containing HAF N 330 prepared from a smoked sheet and from a SMR CV 50

Fig 16.Variations of the elastic shrinkage in function of those of the Mooney's consistancy of mixtures containing the HAF N 330 black prepared from a smoked sheet and from a SMR CV 50.
