THERMIC PROCESSES IN VULCANISATION MOULDS

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Abstract: During the process of the vulcanized products manufacturing, the mould often changes the temperature of the cavity. The paper presents some contributions in thermo calculation of the vulcanization process of the rubber blend in manufacturing. The calculation depending on the optimum adopted vulcanization technological regime using the vulcanization equipments in an efficient way.

Keywords: footwear, sole, mould, thermo calculation

I. INTRODUCTION

HE rubber footwear soles, depending on manufacturing system, may be obtained through vulcanization processes of the rubber blend straight on the vamps, or as semi finished soles which will be assembled on the vamps using gluing or sewing processes. The vulcanization equipments are various and complex depending on the soles manufacturing process, straight on vamps, or as semi finished soles, on the working posts number placed on the unselected of the aggregate, on the number of colors of the future soles, etc.

During the vulcanization process of the rubber blend into the moulds for the footwear soles manufacturing, a high quantity of heating is necessary because the temperature of the rubber blend must increase till 120°C (so, the process of flowing and the filling up of the cavities of the moulds takes place). In the beginning, up to this temperature, it will be used a certain latent heat for melting sulfur (up to the heat necessary for a continuous increasing of the temperature), for decomposition of the agent which produce pore spaces, etc. It follows a new heating period during the temperature will increase till 150-165°C. Now, the thermo chemic vulcanization process is an exothermic one. Depending on the formulas of the rubber and on the vulcanization time, chemical processes are complex being an actual problem of researches in the field.

The paper presents some results of the authors, studding the thermo chemical processes of vulcanization of the rubber blends into the moulds in footwear manufacturing. There will be presented some aspects about thermo balance of the mould heating and the dynamics of the heating process of the rubber blend.

II. EXPOSITION

II.1. The heating thermo balance

The thermo calculation of the mould heating depending on the direction of the heat flow. The cavity may be heated, as pointed in Fig. 1, only through mould dies and upper die or may be heated through metallic shoe-last. The thermo calculation is for a continuous regime respectively, for a working shift. In this case, the warm necessary for sole heating and vulcanization includes the heat lusted in environment.

The heating looses may take place in many ways: by heat conductivity of areas with contacts with mould seat, by convection in environment, on the mould areas contacting with environment, by radiation in environment, by convection on cavities surfaces during the mould is open.

The calculations are based on the classic formulas.

a. The heat calculation for the rubber blend heating is based on [1],[2] equation (1) and it is the necessary heating for the blend temperature increasing from the feeding temperature to the vulcanization temperature:

$$\mathbf{Q}_{\mathbf{a}} = \mathbf{mc}\Delta \mathbf{c} = \mathbf{v}\rho\rho \mathbf{c}(\mathbf{v} - \mathbf{t}_{\mathbf{a}})$$
, Kcal/cycle (1)

where: Q_{a^-} warm for blend heating; m- rubber mass; vmould cavity volume; ρ - rubber blend density; c- specific heat; t_v – vulcanization temperature; t_{a^-} feeding blend temperature.

Knowing that "n" cycles will be realized in one hour, the necessary warm for rubber blend heating one hour, (Q_{ah}) is equation (2):

$$\mathbf{Q}_{\mathbf{a}\mathbf{b}} = \mathbf{n}\mathbf{Q}_{\mathbf{a}} \tag{2}$$

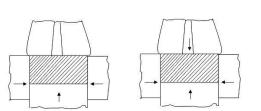


Fig. 1. Meaning heat flow of the heating cavity of the mould

b. The heat lost by conductivity, as pointed in Fig. 2, is sent from the mould to the seat and its calculation is identical with the calculation of the warm which is sent from a warm wall to a cold one [1],[2] equation (3):

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$$Q_c = kS\Delta S = \frac{\lambda}{\delta}S(t_m - t_e)$$
, Kcal/h (3)

where: $Q_{\rm c}\text{-}$ heat sent by conduction; K- coefficient of heat transfer; $\lambda\text{-}$ coefficient of thermo conductivity for the mould material; $\delta\text{-}$ wall thickness; $t_m\text{-mould}$ temperature on heating elements level; $t_e\text{-}$ mould temperature on the seat area.

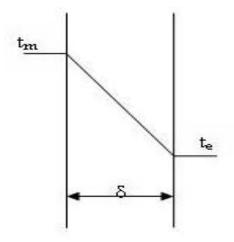


Fig. 2. The heat lost by conductivity

c. The warm lost by convection is given by the warm mould to the environment in two different stages: in all cycle time, by the mould areas contacting the environment and in all time, when the mould is open by cavity area. The warm lost by convection is pointed in [1],[2] equations (4) and (5):

$$\mathbf{Q}_{\mathbf{cv}} = \mathbf{KS}\Delta \mathbf{S} = \alpha \mathbf{S}(\mathbf{t_m} - \mathbf{t_a})$$
, Kcal/h (4)

where: Q_{cv} -warm lost by convection; K- coefficient of heat transfer by convection from the mould to environment; S- mould area contacting the environment; t_m - mould temperature, t_a - environment temperature.

$$\mathbf{Q}_{cv}' = \mathbf{KS}' \Delta t \frac{\mathbf{n\tau}}{60} = \alpha \mathbf{S}' (\mathbf{t}_c - \mathbf{t}_m) \frac{\mathbf{n\tau}}{60}$$
(5)

where: Q_{cv} - warm lost by convection while the mould is open; S - mould cavity area; t_c- cavity temperature; ncycles numbers per hour; τ - time when the mould is opened. The warm lost by convection while the mould is open is a part from total cycle time. This lost may be includes in heating system efficiency, knowing that the time while the mold is open, is short.

d. The warm lost by radiation is on the free mould area and is pointed in [1],[2] equation (6):

$$\mathbf{Q_r} = \mathbf{CFS}\left[\left(\frac{\mathbf{T_c}}{\mathbf{100}}\right)^4 - \left(\frac{\mathbf{T_r}}{\mathbf{100}}\right)^4\right], \text{ Kcal/h} \quad (6)$$

where: Q_{r} - warm lost by radiation; C- coefficient of emission of the mould material; F-coefficient of parallelism; S-mould free area; T_{c} - mould warm wall temperature; T_{r} - environment temperature.

e. Partial warms totalizing

The warm quantity which a heating system must give is pointed in equation (7) which totalizing the warm necessary for the heating of the rubber blends into the mould cavity and the warm lost during one cycle.

$$\mathbf{Q}_{t} = \mathbf{Q}_{a} + \mathbf{Q}_{c} + \mathbf{Q}_{cv} + \mathbf{Q}_{r}$$
(7)

In this balance, the latent heat necessary for physical and chemical processes into the mass of rubber blend was not considered (because, in the beginning, the process has an endothermic character and than the process becomes an exothermic one). Generally, this kind of warm doesn't influence the balance calculations.

II.2. Dynamics of the heating process

When the heating way of the rubber blend is analyzed, there will be considered the following dates [3],[4]: t_m - mould temperature; t_m '- blend temperature mear by the mould; t_a - mould feeding blend temperature; t_a '- blend temperature at the end of the vulcanization process; δ - thickness of the rubber layer; c- rubber specific heat; λ - rubber blend coefficient of heat transference; τ - heating time; S- heating transference area; ρ - specific mass of the rubber.

Transference warm in continuous regime, Q_{t} is pointed in [1],[2] equation (8):

$$\mathbf{Q}_{\mathbf{t}} = \mathbf{K}\mathbf{S}\Delta\mathbf{S} = \frac{\lambda}{\delta}\mathbf{S}\Delta\mathbf{t}$$
, Kcal/h (8)

In a small time, $d\tau$, the transference heat through a layer having a *x* thickness is pointed in [1],[2] equation (9):

$$dQ_{t} = \frac{\lambda}{\rho} S(t_{m}' - t_{a}) d\tau = \frac{\lambda}{x} S(t_{m}' - t_{a}) d\tau \qquad (9)$$

Considering a rubber volume, defined by a *S* area and a dx thickness [4], the warm quantity necessary for the rubber heating, dQ, from temperature, t_a , to temperature, t_a , is pointed in [1],[2] equation (10).

$$dQ_{c} = mc\Delta c = v\rho\rho c(a - t_{a}) = Sdx\rho dx (a - t_{a})$$
(10)

The two warm quantities must be equal in time $d\tau$. Equalization (8) and (9) equations, it will obtained equation (11):

$$\frac{\lambda}{\mathbf{x}} \mathbf{S}(\mathbf{t_m} - \mathbf{t_a}) d\tau = \mathbf{S} d\mathbf{x} \rho d\mathbf{x} \frac{\mathbf{t_a}}{\rho} - \mathbf{t_a}$$
(11)

Using equation (11), $d\tau$, is pointed in equation (12):

$$d\tau = \frac{\rho c}{\lambda} \frac{(t_a - t_a)}{(t_m - t_m)} x dx$$
(12)

The rubber layer heating in entire thickness $\delta_{,}$ (from 0 to $\delta_{,}$ is pointed in equation (13):

$$\tau = \frac{\rho c}{\lambda} \frac{(t_a - t_m)}{(t_m - t_a)} \int_0^{\delta} x dx = \frac{\rho c}{\lambda} \frac{(t_a - t_a)}{(t_m - t_a)} \frac{\delta^2}{2}$$
(13)

So, it is obviously that, the time necessary reaching temperature, t_a' , depends on δ^2 . This time is as big as the rubber layer thickness is bigger [5],[6].

III. EXPERIMENTAL PART

The manufacturing process of footwear soles is a complex problem, depending on the different thicknesses [7],[8] of the rubber blend from heel in comparison with the rest of the sole.

In a certain case of a footwear sole, as pointed in Fig. 3, with a sole thickness equal with 0,01m, a heel thickness equal with 0,03 m and values for the following parameters: $\rho - 1,5 \cdot 10^3$ Kg/dm³; c - 0,33 Kcal/Kg⁰C; λ - 0,14 Kcal/Kg⁰C; δ - 0,01 m; t_m- 175^oC; t_a- 80^oC; t_a- 160^oC; (t_a-t_a) = 160-80=80^oC; (t_m-t_a) = 175-80 = 95^oC, using equation (13), the time is, $\tau = 9$ minutes.

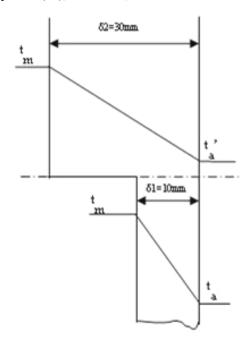


Fig. 3. Schematic representation of a shoe footwear

Following the algorithm for the vulcanization process of one sole having a thickness equal with 10 mm and a thickness of heel equal with 30 mm, for the time of heating and vulcanization of rubber blend is equal with 9 minutes. This time is not technological accepted. So, the heating process in the footwear soles vulcanization must be reconsidered. During the soles vulcanization, the thermo flux is leaded on normal directions to the mould cavity. In these conditions the distance of the flux is different from the distance from the mould till the middle of the heel in the heel area. On the designed sole in horizontal and vertical plane, the distances are a little bit smaller. It was observed that for an interior point, its heating is the sum of minimum two directions of thermo flux normal leaded to the product. So, the heating time is less than the theoretical one.

The time may be different depending on the mix recipe. Depending on the type and percentage of the vulcanization promoters, it is possible to obtain blends with a rapid vulcanization or a slow one.

For the decreasing of the vulcanization time it is necessary to use different rubber blend in heel area and in the rest of the sole. In the heel area it will use a blend with a lower vulcanization temperature and in the rest of the sole, a rubber blend with a higher one. Another way decreasing time, used especially in footwear in manufactured on shoe-last and vulcanized in vulcanization with warm air equipments, is the using of a pre vulcanization process of the rubber blend used for heel area. I this way, during the real sole is vulcanized, the sole in heel area is vulcanized, too, until a complete vulcanization of the heel. The pointed technological solutions don't change the vulcanization regime and they allow only to differentiate the two areas of the sole from the vulcanization chemical point of view. For solving this problem it will be reconsidered the heating processes in connection with the reaction warm. Around the temperature of 120° C, the process is endothermic, the heating being absorbed for the sulphur melting and for the porosity agents decomposing. So, for a certain period of time the heating speed will be decrease. This effect is not a very intense one because, normally, the sulphur percentage is about 2% and the sulphur fusion warm is 10cal/g. For 1 cm³ having 1,5 g, with a 0,03 g sulphur quantity, the warm consumption is about 0,3 cal. In the same time with the vulcanization process beginning, the freedom of the reaction warm generates an important thermo effect because when the sulphur is stabilized as rubber sulphur, the free warm is approximate 412 cal for 1g of rubber. The percentage of rubber sulphur is small for 2% sulphur. So, it will be considered the warm produces depending on the stabilized sulphur quantity, as pointed [1],[2] in Fig. 4.

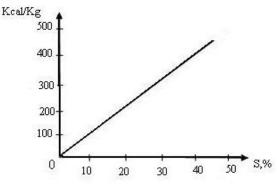


Fig. 4. The influence of sulphur heating the mixture

The warm produces in blend mass will accelerate the heating process, but not enough for allowing an acceptable technology. But, there is another problem, too: for a heating time τ_1 , the temperature of the rubber layer contacted the mould wall, t_m , is a little bit different from the mould temperature. The area opposite to the

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mould has the temperature, t_a , which is higher than the rubber blend feeding temperature. In this case, after a time, τ_1 , for a distance, *x*, from the mould and for a layer having a infinitesimal thickness, dx, the temperature will be, t_i .

After a period, $\tau_{1,}$ just before reaching the vulcanization temperature in all rubber blend mass, the footwear with sole is unloaded from the mould and than the sole is cooled. During the cooling the thermo flux has two directions: a warm quantity goes from the sole to the environment by convection and another quantity goes from the middle to the cooled area of the sole. The temperature, t_i , is for entire mass in equilibrium. From this moment the temperature begins to decrease giving warm to the environment till the equilibrium is reached.

Making a comparison between the intensity of the two thermo fluxes, it observes that thermo flux rubber-air (transference by convection) is lower than the rubber flux warm wall-cold wall. So, in a period of time, $d\tau$, thermo fluxes to exterior and to interior are pointed in equations (14), (15):

$$\mathbf{Q_i} = \mathbf{K_1} \mathbf{S} \boldsymbol{\Delta_1} \mathbf{t} \mathbf{d} \boldsymbol{\tau}$$
, Kcal/h (14)

$$\mathbf{Q}_{\mathbf{e}} = \mathbf{K}_{2} \mathbf{S} \boldsymbol{\Delta}_{2} \mathbf{t} \mathbf{d} \boldsymbol{\tau} \,, \, \mathbf{K} \mathbf{c} \mathbf{a} l / \mathbf{h} \tag{15}$$

Considering that, in time, this two processes will provide the minimum vulcanization temperature, t_v , on all sole section, the layer contacting the mould will have a temperature, t_m ', which in cooling process provides in time a temperature, t_v , in all mass, even a part of this warm is given to the environment.

The cooling time doesn't influence the intensive using of the mould. A superficial cooling of the sole provides the handling and the interior warm which is uniform zed ends the vulcanisation process.

IV. CONCLUSIONS

- 1) The manufacturing process of footwear soles problem vulcanization of rubber is a complex problem, depending on the different thicknesses of the rubber blend from heel in comparison with the rest of the sole.
- 2) The time may be different depending on the mix recipe. Depending on the type and percentage of the vulcanization promoters, it is possible to obtain blends with a rapid vulcanization or a slow one.
- 3) For the decreasing of the vulcanization time it is necessary to use different rubber blend in heel area and in the rest of the sole. In the heel area it will use a blend with a lower vulcanization temperature and in the rest of the sole, a rubber blend with a higher one.
- 4) Another way in decreasing time, is the using of a pre vulcanization process of the rubber blend used for heel area. I this way, during the real sole is vulcanized, the sole in heel area is vulcanized, too, until a complete vulcanization of the heel.

- 5) Around the temperature of 120°C, the process is endothermic, the heating being absorbed for the sulphur melting and for the porosity agents decomposing. So, for a certain period of time the heating speed will be decrease.
- 6) In the same time with the vulcanization process beginning, the freedom of the reaction warm generates an important thermo effect because when the sulphur is stabilized as rubber sulphur, the free warm is approximate 412 cal for 1g of rubber. So, it will be considered the warm produces depending on the stabilized sulphur quantity.
- 7) The warm produces in blend mass will accelerate the heating process, but not enough for allowing an acceptable technology.
- For a heating time τ₁, the temperature of the rubber layer contacted the mould wall, t_m', is a little bit different from the mould temperature.
- 9) During the cooling the mixture of rubber the thermo flux has two directions: a warm quantity goes from the sole to the environment by convection and another quantity goes from the middle to the cooled area of the sole. The temperature, t_b is for entire mass in equilibrium. From this moment the temperature begins to decrease giving warm to the environment till the equilibrium is reached.
- 10) The cooling time doesn't influence the intensive using of the mould. A superficial cooling of the sole provides the handling and the interior warm which is uniform zed ends the vulcanisation process.

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