Theoretical calculations of mechanotermic destruction process with regard to general rubber goods

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Abstract. Reference data on the properties of rubbers and some fillers included in their composition are considered. Based on them, the values of electric and thermal power necessary for the processing of waste tires and other rubber products are calculated. The calculations showed the undoubted advantage of the mechanothermal destruction of rubber products in comparison with the classical pyrolysis methods.

1. Introduction

As known, new methods require new theoretical assumptions. The processing of rubber products by pyrolysis (heating to decomposition temperature without air access) has existed since the beginning of the use of rubber on an industrial scale. Relatively recently, about ten years ago, the idea arose to combine the pyrolysis of rubber wastes with their simultaneous grinding [1]. The theoretical prerequisite for our idea was the high value of the viscosity of rubber products, and, therefore, a rather large value of the coefficient of friction caused by the presence of cross-links in the polymers of this class.

Since this method combines mechanical abrasion of the polymer (mechanical destruction [2-5] and pyrolysis (heating the rubber before decomposition without access of air), we propose the following general name for it: mechanothermal destruction of polymers.

All modern technologies and equipment for the processing of worn-out tires and other rubber products have the following unrecoverable flaws:

- the bulkiness and metal consumption of equipment, which increase exponentially with increasing volume of rubber;
  - low productivity due to loss of time for loading, unloading and pumping of pyrolysis products from the reactor;
  - inefficient heating due to periodic cooling during unloading (heat losses are proportional to the square of the sizes);
- the complexity of the design of the devices of loading, unloading and heating;
- the need for sealing equipment for pyrolysis;
- the need to grind products to the required size;
- a long, expensive process of designing various specialists of the original parts of technological equipment - the reactor, pressurized valves, loading and unloading mechanisms, etc.

The proposed technology of mechanothermal degradation of rubber lacks the drawbacks that are common in the conventional method of rubber pyrolysis. The material is subjected to mechanical stress. In this case, the process of "internal friction" occurs, causing a sharp increase in temperature to values of 450-500 °C, at which the process of rubber pyrolysis begins [1]. To ensure the irreversibility of the decomposition process, the reaction products are removed from the destruction zone. At the same time, their temperature drops to a value of 120-150 °C. They are further cooled and condensed in a special device and processed in the usual manner.

In 2009-2010, we created an experimental installation for the processing of automobile rubber, described in [1]. The operation of such installation has not only evidenced the undoubted prospects of the proposed method, but also has revealed a number of significant flaws. One may say that we achieved the results by trial and error. Thus, there is a need to develop theoretical foundations of a new method for rubber goods processing.

1.1. Analysis of the literature.
Since the existing scientific sources do not even mention our proposed method of rubber processing, we came to the conclusion that some reference data should be collected on the composition and construction of rubbers, as well as the effect of fillers, volatilizers and other chemical agents on their properties [2-6]. Some data are summarized in the table (table 1).

| Table 1. Some reference data on rubber processing. |
|-----------------------------------------------|
| Size, dimension                              | Rubber | Volcanizate | Volcanizate + C | Carbon |
| Density, kg/m³                               | 1050   | 1200        | 1227            | 1400   |
| Coefficient of thermal conductivity, λ, W/m·K | 0.130  | 0.167       | 0.248-0.293     | 0.85-0.91 |
| Thermal diffusivity, a·10⁸, m²/sek            | 8.9-9.0| 11.5-13.0   | 17-20           | –      |

The specific heat, density, thermal conductivity and thermal diffusivity are related as follows [4]:

\[ C_p = \frac{\lambda}{\rho \cdot a} \cdot \left[ kW\cdot s \right] (1) \]

At the same time, the thermal conductivity of rubber varies depending on the content of carbon black according to the following formula:

\[ \lambda_{rubber} = \lambda_0 + K_\lambda \cdot \omega (2) \]

where \( \omega \) is the mass fraction of carbon black; \( K_\lambda \) - is a correction coefficient \[ \frac{W}{m \cdot K \cdot \omega} \].

The values of the correction coefficient \( K_\lambda \), which depends on the brand of carbon black, are presented in the table below (table 2).

| Table 2. The dependence of the values of the correction factor on the brand of carbon black. |
|-------------------------------------|
| Carbon black brand | K-354 | P-234 | P-324 | P-514 | P-803 |
| \( K_\lambda \cdot \frac{W}{m \cdot K \cdot \omega} \) | 0.00151 | 0.00203 | 0.00227 | 0.00235 | 0.00216 |
1.2. The purpose of the article.
Based on the analysis of the reference data, we intend to calculate the amount of thermal (electrical) energy required for mechanothermal destruction of rubbers. Based on the heat balance of the process of their processing, we aim to show the prospects of this pyrolysis method.

1.3. Summary.
Using formula (2), we calculated the changes in the coefficient of thermal conductivity of polyisoprene rubbers, depending on the content and type of carbon black used as a rubber filler, to increase the hardness of tire treads, increase their wear resistance and other useful qualities. The results are presented both as a table (table 3) and as a graph (figure 1).

| Table 3. Thermal Conductivity Values $\lambda$. |
|-----------------------------------------------|
| Brand of carbon black | K-354 |
| Mass fraction of carbon black, % | 0 | 10 | 20 | 30 | 40 |
| Coefficient of thermal conductivity $\lambda$, W/m·K | 0.167 | 0.182 | 0.197 | 0.212 | 0.227 |
| Brand of carbon black | P-234 |
| Mass fraction of carbon black, % | 0 | 10 | 20 | 30 | 40 |
| Coefficient of thermal conductivity $\lambda$, W/m·K | 0.167 | 0.187 | 0.207 | 0.227 | 0.247 |
| Brand of carbon black | P-324 |
| Mass fraction of carbon black, % | 0 | 10 | 20 | 30 | 40 |
| Coefficient of thermal conductivity $\lambda$, W/m·K | 0.167 | 0.190 | 0.212 | 0.235 | 0.257 |
| Brand of carbon black | P-514 |
| Mass fraction of carbon black, % | 0 | 10 | 20 | 30 | 40 |
| Coefficient of thermal conductivity $\lambda$, W/m·K | 0.167 | 0.188 | 0.208 | 0.229 | 0.249 |

As a result of the analysis of the obtained data, we calculated the difference in the values of the thermal conductivity coefficient. For some types of rubbers, the difference in $\lambda$ values, depending on the content and brand of carbon black, can reach a maximum of 56% compared to unfilled vulcanizate. Accordingly, a significantly greater amount of heat should be spent to heat such a rubber filled with carbon black. According to formula (1), we determined the boundary values of the heat capacity of rubbers of this type:

$$C_p = \frac{\lambda}{a \cdot \rho} = \frac{0.167 \div 0.261}{1.85 \div 1.227} = (736 \div 1150) \left[\frac{kW \cdot s}{kg \cdot K}\right]$$  \( (3) \)

With an increase in temperature for every 100 °C, the heat capacity increases by approximately 15% [6]. Thus, since the temperature of the rubber increases by approximately 400 K, it is possible to calculate the change in heat capacity during the heating process according to the following formula:

$$C_p = \frac{C_p^0 + 1.15C_p^0 + 1.30C_p^0 + 1.45C_p^0 + 1.60C_p^0}{5}$$

$$C_p^0 = 736 \div 1150 \left[\frac{kW \cdot sek}{kg \cdot K}\right]. \quad (4)$$
Figure 1. Graphic dependence of the coefficient of thermal conductivity on the content and brand of carbon black.

Substituting in formula 3 the boundary values of heat capacity of rubbers obtained from the calculation according to formula 1, we obtain the following range of heat capacity for this type of rubber:

\[
\overline{C_p} = \frac{[736 \div 1150] + [846 \div 1323] + [957 \div 1495] + [1067 \div 1667] + [1177 \div 1840]}{5} = 957 \div 1495 \left(\frac{kW \cdot s}{kg \cdot K}\right)
\]

The obtained range of heat capacity of filled rubbers is quite wide, but since values of the same order are obtained, it is possible to calculate the energy consumption necessary for processing a unit mass of rubber goods for depolymerization products. To do this, we convert W·s to kW·h and get the following range of values:

\[
W_i = \frac{(957 \div 1495)}{1000 \cdot 3600} = (2.66 \cdot 10^{-4} + 4.15 \cdot 10^{-4}) \left(\frac{kW \cdot h}{kg \cdot K}\right)
\]

Therefore, it takes 0.266 to 0.415 watts of electrical energy to heat 1 kg of rubber per 1 K. Thus, to heat 1 kg of rubber to 500 °C (note that depolymerization process does not require more than this), a minimum of 0.133 to 0.208 kW·h of electrical energy would have to be spent.

The process of mechanothermal destruction has another significant difference from conventional rubber pyrolysis. With a gradual increase in temperature due to mechanical stress, those bonds in the polymer that have the least strength are the first to break. In this class of polymer compounds, a disulfide group, which crosslinks the polymer molecules into a three-dimensional network, has the lowest value of dissociation energy of in the. Some values of dissociation energy are given in the table (table 4).
Table 4. Dissosiation energies [7].

| Type of bond                        | Dissociation energy, kJ / mol |
|-------------------------------------|-------------------------------|
| Hydrogen-hydrogen                   | 432                           |
| Carbon-carbon (single)              | 345.6                         |
| Carbon-carbon (dual)                | 602 ± 21                      |
| Carbon-sulfur (single)              | 272                           |
| Methyl-carbon (–CH₃→–CH₂– + H)      | 142 ± 4                       |
| Methylene-carbon (–CH₂– →–CH= + H)  | ≈ 382                         |

As can be seen from the data in the table, the carbon-hydrogen bonds of the terminal methyl group and the single carbon-sulfur bond have the smallest breaking energy. The percentage of bonds of the first type is extremely small, since such groups are found in polymer molecules, at best, one in 10,000 groups or less. The number of bonds of the second type is directly proportional to the amount of sulfur in the polymer.

For example, with a sulfur content of 1% in rubber, each kilogram of polymer contains 10 g of sulfur. Considering that each sulfur atom is associated with one carbon atom, we find that the amount of substance of the carbon-sulfur atomic groups is 0.3125 mol for each percentage of sulfur. Since it takes 272 KJ of energy to break each mole of carbon-sulfur bonds, only 85 KJ is consumed per percent of sulfur. This amounts to 0.0236 kW·h of electrical energy, respectively. The figure (drawing 2) shows the boundary values of the increase in the values of electric energy for the pyrolysis of rubber, depending on the sulfur content. From the figure it follows that at high sulfur contents (from 5-6% and higher), the energy consumption can double, and even triple at a sulfur content of more than 10%. Since automotive rubber can contain up to 18-20% sulfur (in truck tires), and for heavy vehicles the mass fraction of sulfur can reach 28-30%, a sharp increase in power consumption should be taken into account when pyrolyzing such rubber.

Figure 2. Dependence of the average power of rubber pyrolysis on the sulfur content.
Since the boiling point of sulfur is 440 °C, all atomic sulfur obtained in the pyrolysis process is released in the form of vapors into the expansion chamber of the unit, i.e., the energy spent on dissociating carbon-sulfur bonds is irrevocably consumed.

As for the dissociation energies of single carbon-carbon bonds (table 4, No. 2) and the removal of hydrogen from the methylene units of the polymer (table 4, No. 6), this energy is compensated by the formation of hydrogen molecules (table 4, No. 1) and the formation of large quantities of carbon black, in which only carbon-carbon bonds are present. The energy of such bonds is lower than in the polymer, but a large number of them are formed.

Another important factor affecting the energy consumption during mechanothermal decomposition of rubber is the heat loss by pyrolysis products of the heat generated as a result of the polymers destruction. Since the temperature of the pyrolysis products that are removed from the expansion chamber is 100-120 °C, then, therefore, about 25% of the power spent on processing rubber goods is lost in the form of thermal energy. Thus, based on the target of research (worn-out automobile tires) that contain, in addition to rubber, from 3 to 5% sulfur and about 15-20% of carbon black, and also, taking into account heat transfer by pyrolysis products, we can calculate average power consumption of electric energy required for mechanothermal processing of this type of rubber goods.

The average value of the heat capacity of rubbers of the indicated content with a vulcanizing agent (sulfur) and carbon black is:

\[ C_p = 1226 \left( \frac{W_s}{kg} \right) \]  

which corresponds to 0.31 ± 0.04 kWh of electrical energy consumption per 1 kg of rubber if heated to 450 K.

As a comparison, with the usual pyrolysis method, the energy consumption is about 1.75 kcal for heating 1 kg of rubber per 1 K [8]. If converted to electric power units (when heated to 450 K), it is about 0.9 kWh per 1 kg of rubber.

2. Conclusion
The calculations evidenced the undoubted promise of the new method of processing worn rubber products. The obtained values of power consumption are 3 times less than in the conventional rubber pyrolysis, which confirms the effectiveness of this new method of solving the global environmental problem of our time.

In the future, we contemplate to create a full cycle installation for mechanothermal destruction of used car tires and other rubber products obtaining clean end products.

3. References
[1] Ametov I E and Obolonsky V V 2011 Pyrolysis of rubber by the method of "internal heating"  
Scientific notes of the Crimean Engineering and Pedagogical University (Engineering: Simferopol) 29 8-11
[2] Tager A A 1968 Physicochemistry of polymers (Moscow: Chemistry) p 536
[3] Shur A M 1981 High molecular compounds (Moscow: Higher School) p 656
[4] Tugov I I and G I Kostrykina 1989 Chemistry and physics of polymers (Moscow: Chemistry) p 432
[5] Baramboim N K 1978 Mechanochemistry of macromolecular compounds (Moscow: Chemistry) p 362
[6] Makhlis F A 1989 Terminological reference for rubber (Moscow: Chemistry) p 400
[7] Efimov A I Belorukova et al 1983 Properties of inorganic compounds (Moscow: Chemistry) p 392