STUDIES ON RUBBER BASE IMPRESSION MATERIALS

[PART XV] INVESTIGATIONS ON THE PLASTICITY AND PERMANENT SET ON THE WAY TO BECOME THE ELASTOMER

BY

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INTRODUCTION

Among the various properties of the rubber base impression materials as well as the other elastic impression materials in general, the most important character that they have to provide would perhaps be the good plasticity, i.e., the high degree of elasticity and the low effect in the permanent set of strain.

We must particularly bear in mind that the characters that we require on those impression materials are not on the final products, but upon the way of converting to the final state of the elastomers.

The investigations about such intermediate states of the substances would be very difficult in many cases, especially when the changing rate of the state becomes faster as just seen in the case of impression materials.

The author has endeavoured to overcome such difficulties to pursue the above mentioned objects, despite the results could not always be sufficient.

EXPERIMENT I

Measurements of the plasticity, elasticity and permanent set about the completely cured polysulfide rubber.

1. Apparatus and Method of the Experiment

The apparatus employed in this case of the experiment was so called "Pusey and Jones' plastometer", by which one kilogram statical load is given upon the surface of the cylindrical test piece of 35 mm in diameter and 12.5 mm in height, through a steel semi-sphere plunger of 3.5 mm in diameter.

At the beginning of the measurement, it is usual to set the steel plunger being inserted into the test piece until the hand or the indicator of the dial gauge that shows the sinking depth of the plunger in 1/100 mm unit
penetrates 300 units (3 revolutions) into the test piece.

The *Pusey and Jones* elasticity or hardness $H_4$ is given by the sinking depth of the dial gauge obtained after 60 seconds loading, and the permanent set $H_2$ is also given by the recording when the load is taken off by the load arrester.

The *Pusey and Jones* plasticity $P$ is calculated by the following formula;

$$P = \frac{H_0 - H_2}{H_2 - H_1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

where $H_0$ represents the thickness of the test piece (12.5 mm).

2. Results of the Experiment

The results of the experiment is shown by the Table 21, by which the composition of each material is also noted.

Refering to the Table 21, following items have been understood.

i) The product of the No. 2 experiment was particularly very good in the property of permanent set.

This is considered to be founded in the mixing of the silica fillers of superior quality in the adequate amount.

ii) The product of No. 3 experiment showed the largest permanent set, and this is thought to be chiefly resulted by the mixing of dibutyl phthalate. Thus we have to take cares especially on the mixing of such pasticizers.

**Experiment II**

*Permanent set and plasticity diagrams*

1. Method of the Experiment

The apparatus employed in this case is the same as Experiment I, but in this case, the initial set of the plunger was controlled at the point of 100 units plunged depth and the time of loading was shortened to 30 seconds in each observation in order to enable the quick measurements as well as to know the change of properties in the earlier state. Each experiment was continued during 30 minutes, plotting the records in the interval of two minutes.

The author wishes to represent the records of this case by the following formula (2), distinguishing from the formula (1) of previously given;

$$P = \frac{k_0 - k_2}{k_2 - k_1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

where each record is described by the small letter.

2. Results of the Experiment
Table 21. Elasticity (Hardness), Permanent Set and Plasticity about the Cured Polysulfide Rubber

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Composition of the materials</th>
<th>Measurement about the product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A—agent</td>
<td>B—agent</td>
</tr>
<tr>
<td></td>
<td>P.S.</td>
<td>ZnO</td>
</tr>
<tr>
<td>1</td>
<td>62</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>74.6</td>
<td>5</td>
</tr>
</tbody>
</table>

Explanation for abbreviations in Table 21:
P.S. - polysulfide liquid polymers (about 4,000 in molecular weight)
D.P. - dibutyl phthalate

Fig. 66. Permanent Set and Plasticity Diagrams
Conditions of the experiment; room temperature 18°C, relative humidity 60%
Fig. 67. Permanent Set and Plasticity Diagrams
Conditions of the experiment; room temperature 18° C, relative humidity 60%

Fig. 68. Relation between Permanent Set, Plasticity, Elasticity and Temperature
Conditions of the experiment; room temperature 26° C, relative humidity 70%
The compositions of A and B-agents used in this case were as follows:

**A-agent:** polysulfide liquid polymers (about 4,000 in molecular weight) 77%, CaSO\textsubscript{4}·\(\frac{1}{2}\)H\textsubscript{2}O 10%, sulfur (S) 3%

**B-agent:** PbO\textsubscript{2} 13%, MnO\textsubscript{2} 39%, SiO\textsubscript{2} (B)\textsuperscript{1)} 28%, castor oil 20%

Fig. 66 illustrates the changes of the records of \(h_1\), \(h_2\) and \(p\) following the time lapse about the material of the above mentioned combination.

Referring to the figure, it is understood that the records of \(h_2\) and \(p\) show the minimum and maximum at about 18 minutes after the mixing of A and B-agents.

It is considered from this result that the rate of the change of \(h_2\) was so large before 18 minutes from the beginning, thus we have to take it in minds not to take off the impressions from the pattern in such a state.

When we think over that the material employed in this case was thought to have rather faster setting time in comparison to that in the market, and also that such materials are used in the practice in comparatively short time, it would be natural to think such materials have not been yet used in the satisfactory conditions.

Fig. 67 shows the another result of experiment, when the material of following composition was used:

**A-agent:** polysulfide liquid polymers (about 4,000 in molecular weight) 62%, CaSO\textsubscript{4}·\(\frac{1}{2}\)H\textsubscript{2}O 10%, sulfur (S) 3%

**B-agent:** PbO\textsubscript{2} 12.5%, MnO\textsubscript{2} 37.5%, SiO\textsubscript{2} (B)\textsuperscript{1)} 28%, castor oil 19%

This case, too, it has taken about 18 minutes to reach the minimum and maximum of \(h_2\) and \(p\), but their descending and ascending curves appeared almost linearly.

In both cases of (a) and (b) of above mentioned, the conditions of experiment were kept at 18°C in the room temperature and 60% in the relative humidity, as noted on the figures.

**Experiment III**

*Correlations among temperature, permanent set and plasticity diagrams*

Another result of the experiment has been obtained about the material used in the case of (a) of Experiment II, as shown by the Fig. 68.

In this case, the change of the temperature was observed at the same time to investigate the correlations among temperature, permanent set (\(h_2\)) and plasticity (\(p\)) diagrams.

This case of the experiments was taken part in at the room temperature of 26°C and the relative humidity of 70%, as noted on the figure.

As it is clearly understood by the figure, the minimum state of \(h_2\) was resulted after about 13 minutes from the beginning of mixing A and B-
agents. The quick setting rate of this case was, of course, resulted by the uprising of the surrounding temperature.

**Experiment IV**

Correlations among temperature, Shore's elasticity, Shore's hardness, permanent set and plasticity diagrams

Fig. 69 and 70 illustrate the correlations among the temperature, Shore's elasticity, Shore's hardness, permanent set and plasticity obtained simultaneously by the same method as shown in the Experiment II.

In this case, the same material was employed as the case of the Experiment II (i), and the conditions were 18°C in the room temperature and 60% in the relative humidity for the former, and 16°C and 60% for the latter.

![Graph](image)

Fig. 69. Correlations among Temperature, Elasticity, Hardness and Plasticity

Conditions of the experiment; room temperature 18°C, relative humidity 60%
From the results, following items have been concluded.

1. All diagrams except h4 diagram showed the tendency of primary transformation altogether at when the temperature reached the top of its ascending curve, so thus this point that represents the time to reach the summit of the temperature diagram may be called the "primary set".

2. In the Fig. 69, Shore's elasticity showed the maximum several minutes after the "primary set", that time may be called the "secondary set".

In the Fig. 70, Shore's elasticity reached the maximum at the same time with the top of the temperature. So in this case, the "primary" and "secondary set" are assumed to become superposed each other.

3. As seen in Fig. 70, at about 22 minutes from the beginning, Shore's hardness, h2 and p have been reached each minimum and maximum state altogether, so thus the point may be called the "final set".

4. The accommodation of the fluidal state impression materials onto the objects should be done as early as we can do, and the removal of the

![Graph showing correlations among Temperature, Elasticity, Hardness and Plasticity.](image)

Fig. 70. Correlations among Temperature, Elasticity, Hardness and Plasticity

Conditions of the experiment; room temperature 16°C relative humidity 60%
impression be done at least after the "secondary set", it is readily be imagined from the diagrams.

The "primary", "secondary" and "final set" are shown by the wave like lines on the figures.

EXPERIMENT V

Change in elasticity, permanent set and plasticity from the "final set" to the "cure" state

In the cases of Experiment I, II, III and IV, the initial set position of the steel plunger of the Pusey and Jones' apparatus was controlled at the point of 100 units of the dial gauge (1 revolution of the indicating hand) instead of being controlled at the 300 units (3 revolutions of the indicating hand) as executed in the case of ordinary testing of rubbers.

The latter method is thought to be too severe to be used for the impression materials on their way of the setting, because at this time, the 1 kg load acts as the impulse force onto the test piece resisting the elastic force

![Diagram](image)

Fig. 71. Change in properties from the "final set" to "Cure" state
Conditions of the experiment; room temperature 22°C, relative humidity 80%
of the material itself.

Fortunately, the author has found out that the latter method of testing came to be impossible until just when the "final set" had accomplished. Then the author caught the change of the properties after the "final set" by the latter method as shown on the Fig. 71. The material employed in this case was the same as the Experiment IV.

Refering to the figure, following items have been concluded.
1. After the "final set" the newly born elastomer has become to be able to endure the dynamical force caused by the own elasticity at considerably rapid rate by this material.
2. The H, H and P diagrams moved almost parallel, and their beginning portions gradually approach to a line representing the "final set", as illustrated on the figure.
3. The state of the product that shows the minima by the above mentioned observations may be called the "cure".
4. As seen in the ordinary polysulfide curing, we may suppose the case of taking much more times to become completely the fixed states in those properties, when the two steps of the "cure" would be considered, namely the "initial cure" that means the state of almost fixed and the "final cure" that means the state of completely fixed.

DISCUSSION AND SUMMARY

It is thought to be very important to know the behavior to become the high polymer states about such impression materials, because we have to use them on their ways to convert the complete elastomers.

Among various properties, the permanent set would perhaps be the most significant, when we wish to take the more faithful impressions.

It has been very regrettable for the author that few reports had been delivered about such investigations upon the moving states of the materials.

In this report, various measurements have been taken simultaneously to find out the correlations among those records of the measurements, and thus consequently the behavior of the moving state has been caught by the three steps of the setting, namely the "primary", "secondary" and "final set".

Then the author wishes to establish the definitions of the above mentioned steps of the setting in the general meaning, because such discussions would be very important in the practical applications of such materials in comparison to the occasions of the ordinary rubber and the other like materials, when such problems about the moving states of the materials have little meanings.

Heat liberation is almost always seen when the substances do the solidi-
fication, despite the reaction whether be exothermic or not, and that is thought to be caused by the internal transformation of the structure.

Thus it is natural to think that the end of the heat liveryation informs the end of the change of internal structure, when the state of the "primary set" would be caused.

The state of the "secondary set" would certainly be caused by the extermination of the entropy change in the domain of the third law of thermodynamics.

After the "secondary set", the potential energy of the substance would be remained still high by the heat conservation, and this would gradually be taken down to the state of equilibrium with the surrounding condition, when the state of the "final set" would be resulted.

On the occasion of discussing about the problem of setting, the chemical reactions among the ingredients and the internal transformation of the structure caused by the entropy change have been thought to be chiefly concerned, but the another problem would be remained, e.g., the problem of the internal stress.

This would have been conserved as the internal energy in such elastomers, and then the internal stress would be relaxed to the stable state of that substance, when the "cure" state certainly be obtained.

The above mentioned relations would be explained by the following equations: 2) 3) 4)

\[ f = \left( \frac{\partial E}{\partial l} \right)_T - T \left( \frac{\partial S}{\partial l} \right)_T = f_E + f_S \]  \hspace{1cm} (1)

where

- \( f \) ....internal stress given to the substance
- \( l \) ....deformation of the substance
- \( E \) ....internal energy
- \( S \) ....entropy
- \( T \) ....absolute temperature
- \( f_E \) ....energy component
- \( f_S \) ....entropy component

Substitute the Maxwell equation;

\[ \left( \frac{\partial S}{\partial l} \right)_T = - \left( \frac{\partial f}{\partial T} \right)_l \]  \hspace{1cm} (2)

Then the equation (1) becomes as follow;

\[ f = \left( \frac{\partial E}{\partial l} \right)_T + T \left( \frac{\partial f}{\partial T} \right)_l \]  \hspace{1cm} (3)

When the differentiation by the time (t) of \( f_S \) is considered,

\[ \frac{df_S}{dt} = \frac{d}{dt} \left\{ T \left( \frac{\partial f}{\partial T} \right)_l \right\} = 0 \]  \hspace{1cm} (4)

the "secondary set" would be resulted. The change from the "secondary set" to the "final
"set" would be caused by the Joule's effect, when the following equation takes place:

$$\Delta E = f \frac{dE}{dt}$$

Thus

$$\Delta E = C_i \Delta T + \left( \frac{\partial E}{\partial l} \right)_T \Delta l$$

where $C_i$ represents the heat capacity of the substance, when the length is assumed to be constant.

Then

$$\Delta T = \frac{1}{C_i} \left( f - \left( \frac{\partial E}{\partial l} \right)_T \right) \Delta l = -\frac{T}{C_i} \left( \frac{\partial S}{\partial l} \right)_T \Delta l$$

Thus when the decrease of entropy is caused by the elongation of the material, the temperature rising is to be resulted by the adiabatic deformation, then

$$\Delta f = \left( \frac{\partial f}{\partial l} \right)_T \Delta l + \left( \frac{\partial f}{\partial T} \right)_T \Delta T$$

If $f$ is kept as constant, from (8)

$$\left( \frac{\partial l}{\partial T} \right)_f = \left( \frac{\partial S}{\partial l} \right)_T / \left( \frac{\partial f}{\partial T} \right)_T$$

From (9), when

$$\left( \frac{\partial l}{\partial T} \right)_f = 0$$

the "final set" would be accomplished.

Furthermore when the first term of the equation (3) becomes as follow;

$$\frac{df}{dt} = \frac{d}{dt} \left( \frac{\partial E}{\partial l} \right)_T = 0$$

the "cure" state of the materials would certainly be resulted.

From the Experiment I to IV, the record of $h_1$ showed almost the constant value that was the same value as prepared for the initial set. By these results, those experiments would sufficiently be assumed as the constant load testings.

Just reversely, on the occasion of the Experiment V, 1 kg load was responded onto the test pieces resisting their elastic reactions, so in the case of the latter, the test load is thought to be the dynamical one.

We must have especially cares on the facts that the results obtained by each method are remarkably different with the other.

In the case of latter, it was very interesting that $H_1$, $H_2$ and $P$ diagrams were all approaching to the same line, namely the line which shows the "final set".

The author thinks that those results are all the endorsements of the formerly mentioned principles that were derived from the law of thermodynamics as well as the conclusions concerning the correlations between the temperature and setting diagrams in the author's earlier reports.5) 6)

Those problems about the molecular structures as well as the thermodynamical reactions are considered to be difficult, so the author does not
think to find the accurate conclusions at once.

What the author has been endeavouring to find out is how to treat those materials with more rational operations in our practical applications, being acquainted with the more and the more detailed behavior of them.

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