ON THE PHYSICAL PROPERTIES OF SYNTHETIC RESIN CROSS-LINKED IN ELECTRIC FIELD

By

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1. Introduction

As regards electrical conductivity, that of the plastics approaches that of the electronic semiconductors. Both plastics, and semiconductors have many common properties. The conductivity of plastics ranges from 10^0 to 10^{-20} ohm^{-1} cm^{-1} depending both on material and on temperature.

Plastics may be conductors of *n*-type, i.e. hole-, or electronic conductors. They were taken previously as ionic conductors. Some plastics have in fact relatively high ion concentrations, however, with slightly mobile ions. Proton movement could be detected in polyamides.

Experiments on a number of plastics failed to prove mass transfer, though so characteristic for ionic conductivity. On the other hand the Hall effect, characteristic for electron conductivity, could be detected in some plastics. It is rather difficult, in cases even impossible, to demonstrate the Hall effect for most plastics, due to the fact that the conduction currents are extremely small [1].

2. Experiments and results

2.1. Cross-linking in strong electric field

High intensity electric field was produced by a van' de Graaf-generator. The generator's collector is a cylinder of 45 cm length and 17 cm diameter, with two hemispheres of 17 cm diameter each end. An earthed sphere of 17 cm diameter was put in the axis of the cylinder at some distance from the collector end. Sparks up to 16 cm length could be produced between the two bodies indicating an estimated voltage of about 2.5 to 3×10^5 V [2].

The spherical end of the cylinder served as the one electrode of the cross-linking field in order to avoid undesired losses in the generated high voltage. The method of below has been followed.

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A paraffin slab of $40 \times 25 \times 3$ cm size was put at the end of the cylinder. In the slab there was a 5×5 cm hole, and covered inside with plexiglas, in which the liquid resin to be cross-linked was put on a plexiglas sledge, at a distance of 1.5 to 2 cm from the collector. The cross-linking of the resin took place in a thin card box $5 \times 5 \times 1$ cm, impregnated with paraffin. On one side the card box was covered for earthing with an aluminium sheet. The paraffin slab and the plexiglas hole were intended to eliminate discharges against

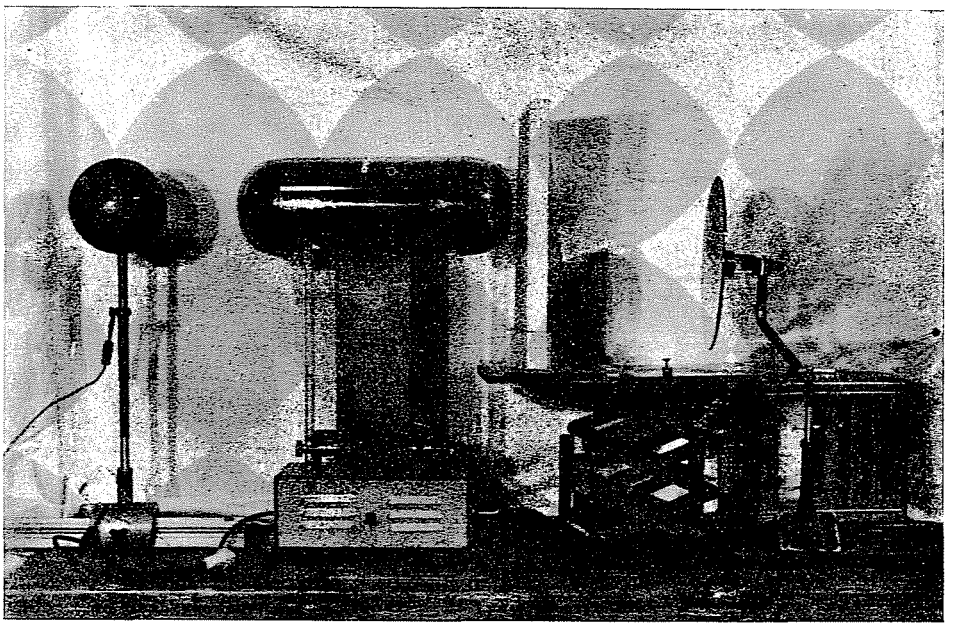


Fig. 1

the sheet. Two samples were made for each cross-linking experiment, one for the electric field, and the other one without it. Samples made this way permitted comparisons of the properties in question.

The arrangement for cross-linking is seen in Fig. 1. The voltage of the generator-cylinder was determined with the aid of the sphere on the left-hand side. The sphere could be moved along an optical bench, the maximum discharge spacing being read off a scale along the bench. These discharge spacings varied from 10 to 16 cm and decreased by 2 to 3 cm during the process of cross-linking. The estimated voltage was over 2×10^5; the field strength within the cross-linked material may be assessed to some 10^4 V/cm.

The card walls of the sample holder box reduced the field strength. In order to minimize this effect, a free surface of the material was arranged against the field direction in the following way. The even liquid resin to be

hardened poured into an open card box, $5 \times 5 \times 1$ cm size, was put below the cylinder of the generator near its end. The field at this place is much the same as applied for the previous cross-linkings. It should be noted that the material could not be placed too near to the collector to prevent it from attracting the material to itself. Even in this case some thin threads were formed between the free surface of the liquid material and that of the cylinder indicating macroscopically the polarizing effect on the material of the field. No doubt, the sample was in a stronger field now than the samples at the earlier cross-linking.

Two sorts of Eporezit F-22, A and B, the same make but of different origin, were investigated, both containing some 9 per cent by weight of hardener Härter-HY951. The cross-linking in electric field lasted some 5 to 7 hours. The material solidified during this time.

The hardened samples were subjected to the following tests:

1 electrical conductivity,

2 light transmission,

3 electret-properties,

4 thermoanalytical investigation.

All these investigations went in parallel on samples (with the same composition) cross-linked in an electric field or not.

The dependence of conductivity and optical properties of the samples on the direction of the cross-linking field was also investigated. Terms "perpendicular" and "parallel" are applied in meaning that in perpendicular tests the electric field or light beam is perpendicular and in parallel tests parallel to the sample-platelet, these being parallel and perpendicular to each other respectively.

2.2. Electrical conductivity and temperature

Setup is shown in Fig. 2. Temperature range: 20 to 240 °C. The samples were put between two platinum plate electrodes between two steel blocks and the whole arrangement was placed in a furnace. In the first phase measurements were taken simultaneously on samples cross-linked in and without electric field, with the aid of three platinum electrodes put between the blocks. Temperature was measured with an iron-constantan thermoelement placed into the upper block. Later the two samples were measured separately. The temperature difference between sample and the block could not be more than 1 to 2 °C. To our experience, the electric conductivity as a function of temperature is expressed by

$$k = A \exp\left(-\frac{B}{T}\right)$$

where A and B are constants, characteristic of the material and T is the absolute temperature. Our results are represented in a graph: log k vs $\frac{1}{T}$. Conductivity results can be summed up as follows.

Fig. 3 shows a case of temperature dependence of conductivities of samples made on material A, and cross-linked with and without an electric field. The conductivity is seen to be greater for a sample cross-linked in a field (curve No 2) than without.

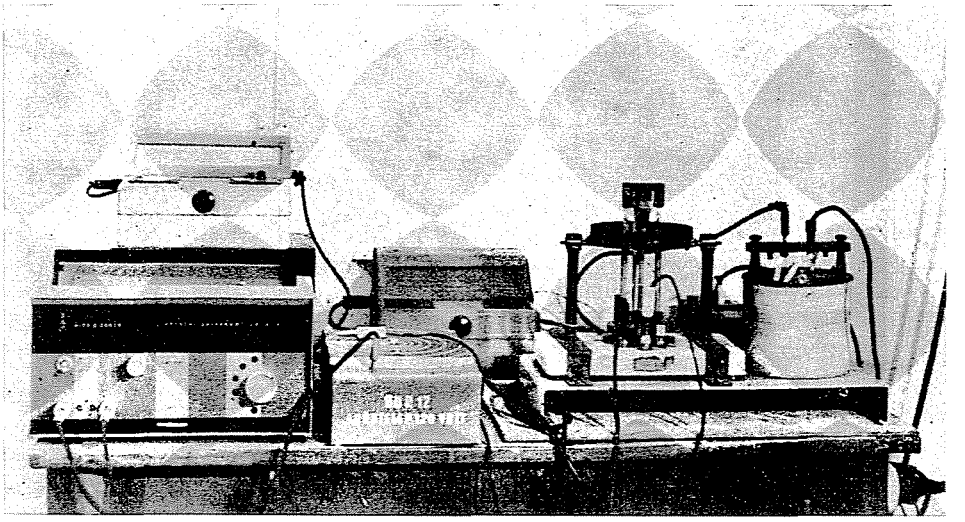


Fig. 2

Fig. 4 shows the dependence upon the direction of field. Curves 2, 3 and 1 represent the perpendicular case, the parallel case, and the conductivity of a sample cross-linked without field, respectively. The conductivity in the perpendicular case is greater. This experiment was carried out on material B. In the middle of the temperature range, 90 to 150 °C, the dependence of conductivity upon temperature is marked. In the lower and higher temperature ranges there is less dependence. Comparison of Figs 3 and 4 shows a difference between materials A and B. In case B the conductivity did not exhibit a slower change at lower temperatures.

This reminds us of the phenomenon well-known in the case of semiconductors that materials of the same kind all show differences in properties sensitive to structure as e.g. electrical conductivity.

Our results have led us to the following statements:

1. samples cross-linked in electric field have higher electrical conductivities,

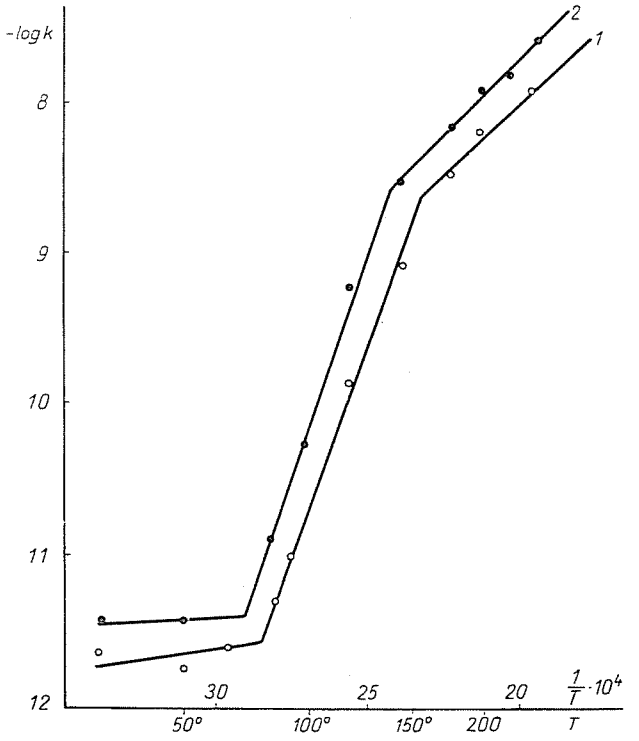
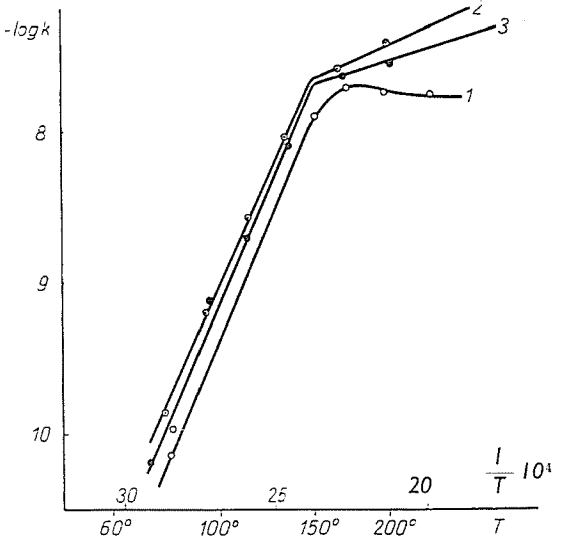

-log k
8
9
10
11
12
2
1
30
25
20
$\frac{1}{T}\cdot 10^4$
50°
100°
150°
200
T

Fig. 3


-log k
8
9
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25
20
$\frac{1}{T}\cdot 10^4$
60°
100°
150°
200°
T

Fig. 4

2. the conductivity depends upon the direction of field for samples cross-linked in an electric field,

3. in the perpendicular case the conductivity is somewhat higher than in the parallel case.

It could be noted that samples cross-linked in an electric field or not, were different in colour. This colour difference could be observed even with unaided eye and appeared at about 170 °C.

2.3. Light transmission of samples

The optical extinction of plastic resin cross-linked with, and without electric field was tested on platelets of $10 \times 10 \times 2$ mm size. Comparisons were made between the extinctions of samples cross-linked with, and without electric field as well as their relation to the direction of field of the extinction.

Two kinds of equipment have been used: the MOM "Spektromom 202" for the 190 to 1300 nm range, and the Soviet UM-2 monochromator of greater resolving power in the 380 to 750 nm subrange. In the latter case the light intensity was measured with a selenium photoelement connected to a Kipp and Zonen galvanometer. The extinction was calculated according to

$$E = \frac{1}{d} \log \frac{I_0}{I}$$

and plotted.

The aim of our first optical measurement was the instrumental demonstration of the difference, if any, between the extinction spectra of the heat-treated samples cross-linked with or without field.

Fig. 5 shows the difference between the extinctions. In the visible spectrum the heat-treated and field cross-linked sample had a greater extinction (curve 2).

Fig. 6 shows the extinction of samples cross-linked with, and without field as well as the dependence on the field direction. Curve 1: sample without field; curve 2: sample parallel to field; curve 3: sample perpendicular to field. There are some differences. In the 1100—1200 nm range the extinction of some samples without field is greater.

Fig. 7 shows the dependence on field direction in the visible spectrum. Curve 1: parallel; curve 2: perpendicular case.

We present finally a further result (Fig. 8) concerning light absorption of samples cross-linked with and without field. The field was produced with two metal electrodes put into the resin. In this case the difference of extinction coefficients is plotted vs. wave-lenght. There are two sharp maxima at wavelengths 400 nm and 1100 nm, respectively. The places of maxima coincide with those of extinction got before.

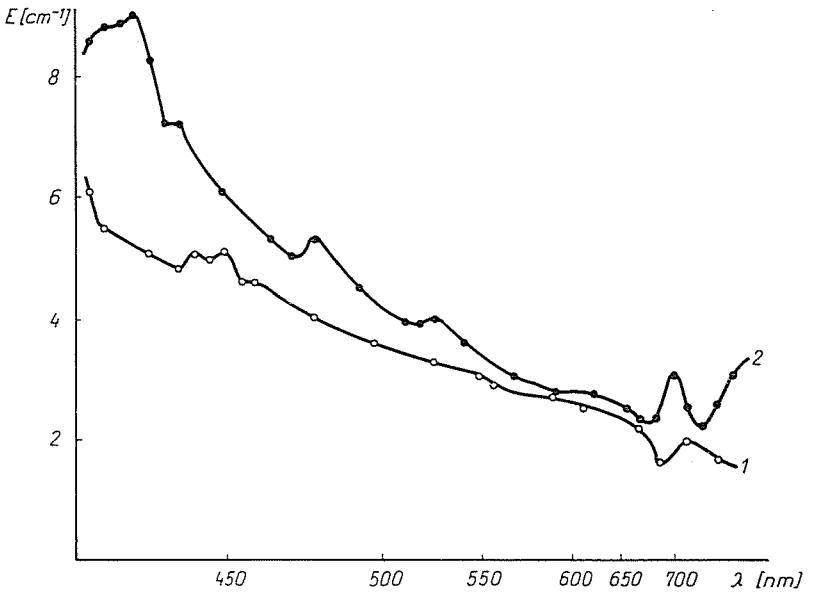

Fig. 5

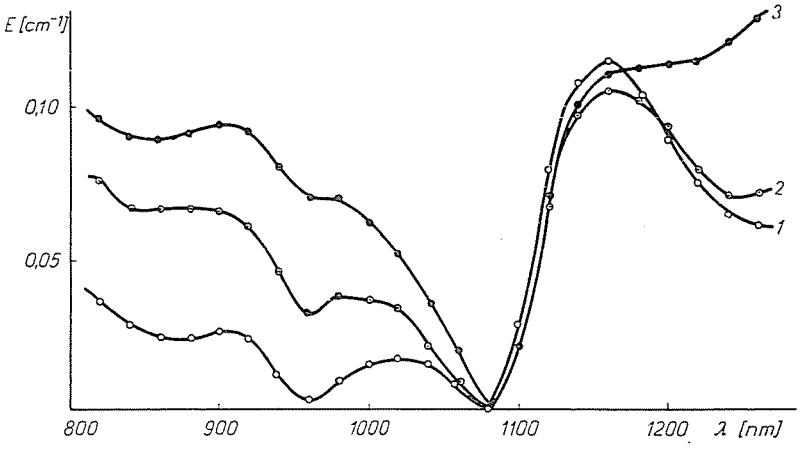

Fig. 6

2.4. Electret properties of plastic resin

The samples exhibited electret properties. The so-called bipolar electrets display opposite but equal charges on two faces, while for unipolar electrets the charge of one face is far greater. In the first days after preparation, the samples were tested in original $5 \times 5 \times 1$ cm size, and not cut before determining their electret properties. Thereafter they got sliced for electrical and optical tests.

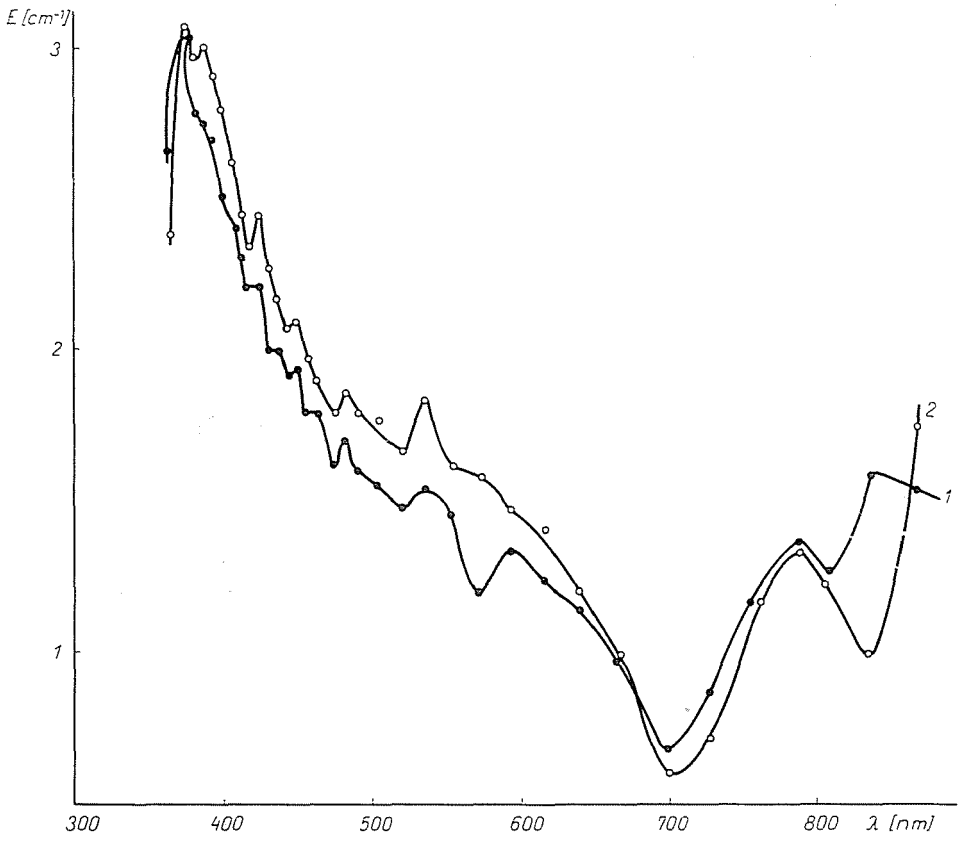
E [cm⁻¹]
3
2
1
300
400
500
600
700
800
λ [nm]
1
2

Fig. 7

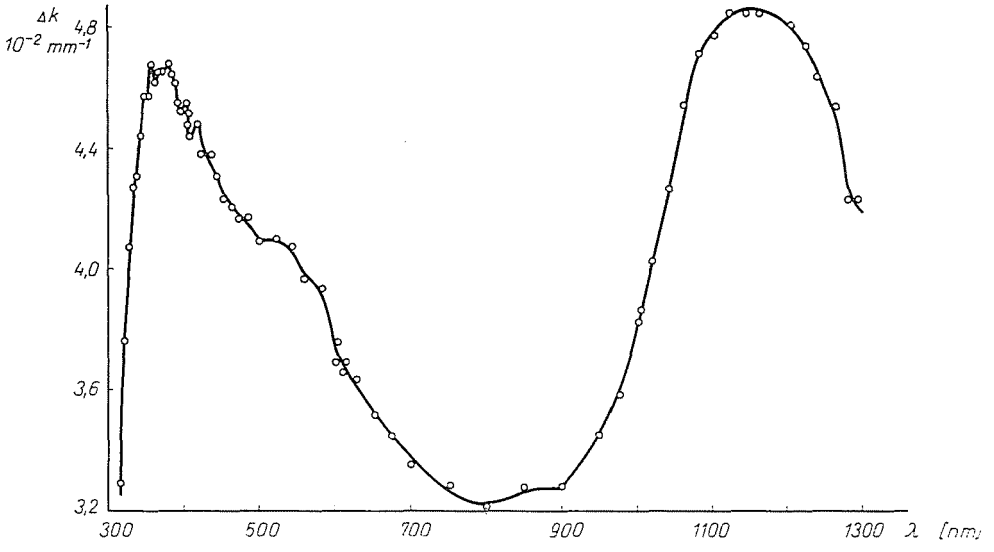
Δk
10⁻² mm⁻¹
4,8
4,4
4,0
3,6
3,2
300
500
700
900
1100
1300
λ [nm]

Fig. 8

Charges can be demonstrated in the following way. First of all the samples were wrapped in metal sheets and kept so for a few days [3, 4].

Unwrapped, the samples were placed on an earthed metal plate. Charges on the face, if any, can be demonstrated like for an electrophorus. A small metal platelet with insulating handle is placed on the sample, the charge of which produces influence in the metal platelet. The free charge is conducted away, and the bound charge is indicated by an electrometer. First samples (material *A*) displayed no charges of not cross-linked field.

In order to investigate the charges closer, a more sensitive, Zeiss projection electrometer was used. For investigation of charges the sample was touched with the point of a pin, the free charge was conducted away, the electrode of the electrometer was touched with the pin and the quantity of charge was indicated by the deviation of the electrometer thread. Charges have been measured at the four edges as well as at the middle of the square face 5×5 cm on both sides of the sample. Samples made of material *A* were in most cases bipolar. The bipolarity of the samples could easily be demonstrated by an electrometer. A foil electrometer has been used. In the case of material *B* — four samples have been investigated altogether — samples cross-linked with and without a field were compared. Samples made without field displayed charges, too. This might be due to the fact that the method applied in the previous case was not as sensitive as that in latter one. All samples but one were unipolar. Samples cross-linked with field showed charges greater by as much as 2—3 times — in extremum cases by 10 to 20 times. Charges in the middle of the samples were the greatest.

2.5. Derivatographic analysis of thermal decomposition of the samples

With respect to the results for samples hardened in, or without field, the investigation of thermal properties of the samples seemed to be advisable. Derivatography was applied to several samples cross-linked with or without field using a MOM-type Derivatograph Paulik—Paulik—Erdey system, a complex thermoanalytical device, where a chosen heating program may be applied to simultaneously recording the temperature (T curve), the enthalpy change (DTA curve), the weight change (TG curve) and the rate of weight-change (DTG curve), of a sample.

Exotherm effect (DTA curve) was seen to be more marked for samples previously hardened in field, than not.

It has been found moreover that activation energies calculated from DTG curves were smaller for samples hardened under field than not. It could be concluded that field concomitant to cross-linking builds in energy into the resin sample which appears as excess exotherm effect during decomposition.

3. Conclusion

The cross-linking of the synthetic resin in electric field leads to a material with different properties. Thus, influencing of a chemical reaction by an external electric field alone has been realized and proved. This fact justifies again the introduction of a new concept to be termed electrical field-chemistry, that has already been suggested [5, 6, 7].

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Summary

Conductivity, electret, optical and thermal properties of a certain synthetic resin hardened by chemical cross-linking in a strong external electric field, have been investigated. The comparative results obtained on samples of the resin hardened under the effect and in absence of the field, testified the effect of the field on the cross-linking process, and therefore on the above mentioned properties of the hardened material. Some properties showed also anisotropy.

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