CENTRAL LABORATORY OF PHYSICO-CHEMICAL MECHANICS

BULGARIAN ACADEMY OF SCIENCES

PROCEEDINGS

10th International Conference
on

MECHANICS AND TECHNOLOGY OF COMPOSITE MATERIALS

September 15 - 17, 2003

Sofia, BULGARIA

Proceedings of 10th International Conference on Mechanics and Technology of Composite Materials
September 15-17, 2003, Sofia, Bulgaria

PLASMA-CHEMICAL SURFACE MODIFICATION

P. Dineff[1], T. Vladkova[2], D. Gospodinova[1], N. Tipova[2]

[1]Technical University of Sofia, 1000 Sofia, Bulgaria
[2]University of Chemical Technology and Metallurgy, 1000 Sofia, Bulgaria

Introduction

Low-frequency barrier discharge (*LF-BD*) at atmospheric pressure (about 0.1 MPa) and low frequency (50 or 60 Hz) does not require an expensive and complicated vacuum system. Therefore it is an alternative of the glow and radio frequency (*RF-*) discharges in the technology of plasma-chemical surface treatment of polymers and polymer materials, [1].

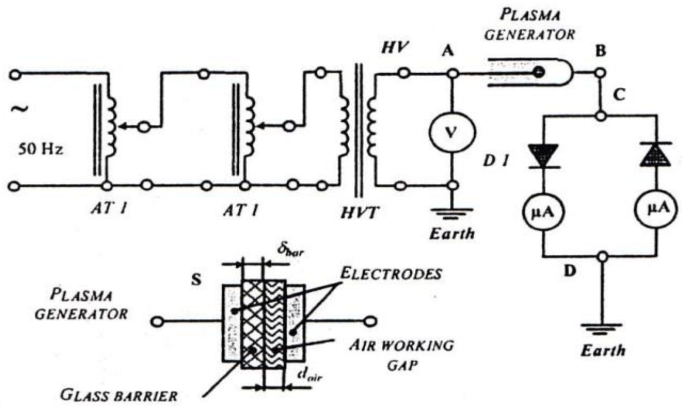


Fig. 1. Electric circuit of the experimental generator for production of cold technological plasma at low frequency (50 Hz) and at atmospheric pressure (of about 0.1 MPa).AT 1 and AT 2 are adjustable transformers for fine regulation of the voltage on the LF-BD discharge; HVT - step-up transformer; D 1 and D 2 – diodes allowing direct measuring of the average value of electric current I_{av} *of LF-BD discharge.*

The burning of the *LF-BD* discharge in air is defined mainly by both the oxygen and nitrogen dissociation and ionization and the plasma-chemical modification – by the generation of both ozone (and chemical active products of its degradation) and nitrogen oxides. The general description and controlling of the plasma-chemical surface modification of different materials is too complicated because of the very large variety of the plasma-chemical processes. That's way an optimization of the operation conditions is necessary when it is applied to any material.

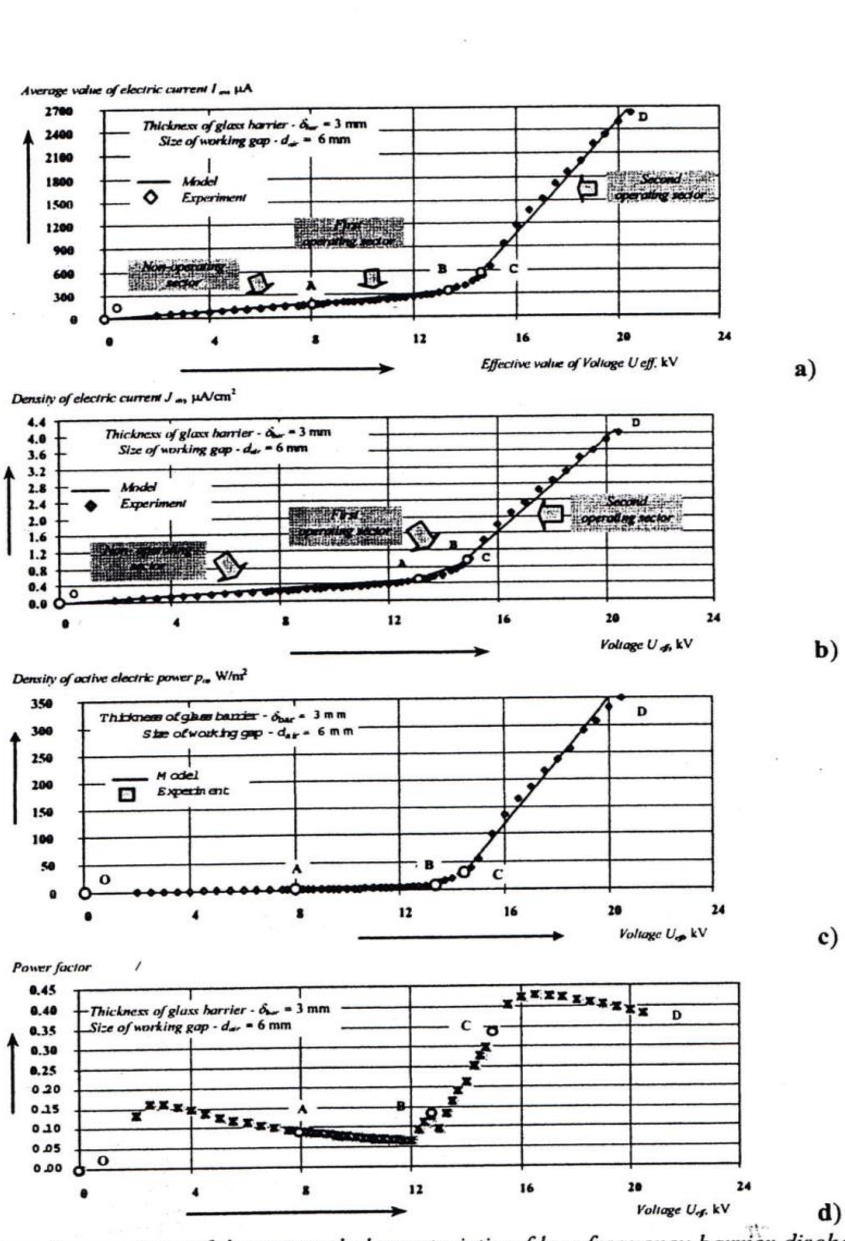


Fig. 2. Operating regions of the external characteristic of low-frequency barrier discharge – the relationship between the average value of current I_{av} and the effective value of applied voltage U_{eff} (a):OA – non-operating sector; AB – first operating sector, namely plasma containing ozone and products from its decomposition; CD - second operating sector, namely plasma containing nitrogen oxides; BC - transient region. Other electric characteristics of the discharge: current density J_{av} (b), surface density of active power p_a of the discharge (c) and the power factor (d) as a function of the applied voltage U_{eff}.

For a long time we and other authors are dealing with the utilization of wood flour (*WF*) through filling of plastics and rubber compounds. It was found that it acts a non-active filler increasing significantly the modulus but usually making worse some other mechanical parameters, [2].

The aim of this investigation is to study the conditions under which the plasma-chemical action of *LF-CD* discharge could be governed by suitable choice of both electrical regime of burning and working media – "dry" air plasma or "wet" ammonia plasma (ammonia vapors). This approach could be illustrated with plasma-chemical modification of *WF* and a study of its reinforcing effect in conventional rubber compounds.

Experimental Investigations and Characteristic of the Discharge

Low-frequency high-pressure barrier discharge (*LF-BD*) owes existing discharge at which capacitive (reactive) resistance of the dielectric barrier (one or two) limits the current in the discharge gap of the plasma generator. The dynamic regime of burning insures large Debye's radius that defines the existence of ideal classic plasma in relative large technological volumes. It has a low temperature – it is cold plasma due to worse both impact interaction and exchange of kinetic energy between the light and heave plasma components. *LF-CD* discharge is the sole discharge producing cold technological plasma at atmosphere pressure – of about 0.1 MPa.

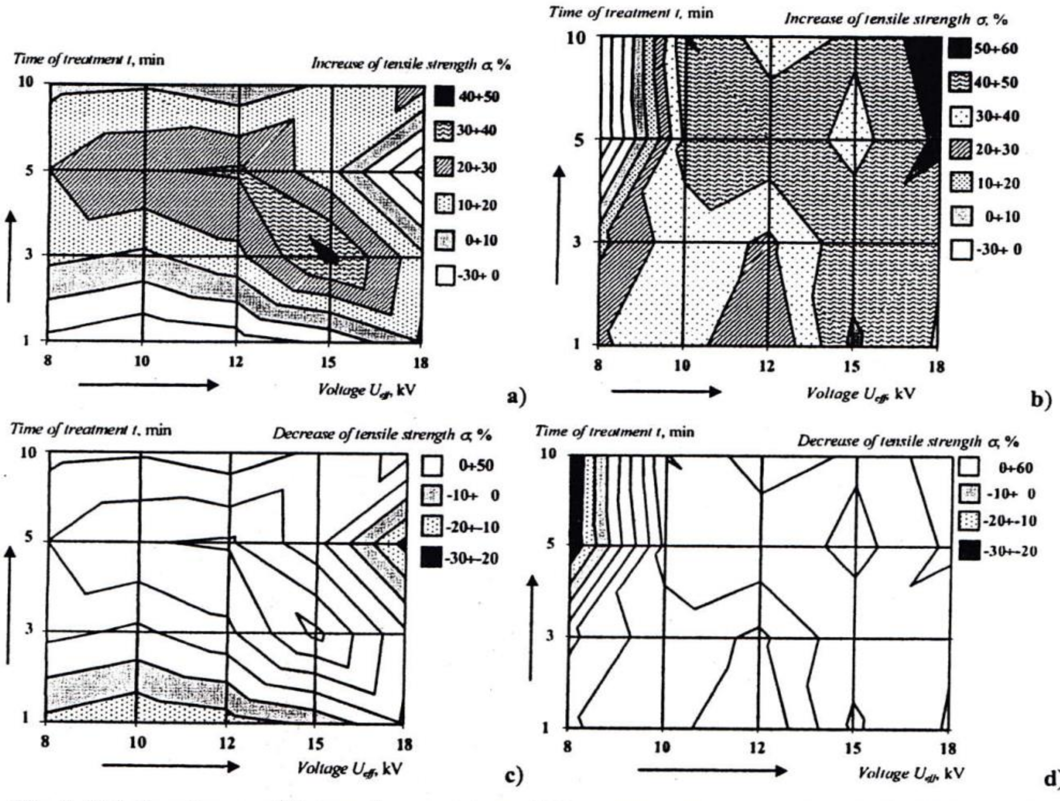


Fig. 3. Relative change of the tensile strength, σ of NR - compounds containing 50 phr WF treated in air (a, c) or ammonia (b, d) plasma obtained in LF-BD discharge. The relative change of the tensile strength σ is towards the tensile strength (σ = 6.0 MPa) of a control NR - compound filled with 50 phr non-treated WF. The tensile strength of the control non-filled NR - compound was of 24.6 MPa.

Our experimental investigations [3, 4] confirm the existence of linear correlation between the quantity of electricity Q, irrespective between the average value of electric current I_{av}, current density J_{av} and the surface density of the active power p_a of the *LF-CD* discharge from the one hand

and the effective value U_{eff} of the applied voltage on the other hand. For the investigated region this linearity is of the functional type and the linear correlation coefficient is of over 0.99, [4].

The external static volt-ampere characteristic of the *LF-CD* discharge obtained experimentally thorough the circuit of Fig. 1, allows to be selected the suitable working conditions of the plasma generator – to generate ozone- and oxygen containing plasma or nitrogen oxides containing plasma. Something more, thorough its derivative characteristics could be evaluated: *the technological efficiency*, fig. 1c - thorough the density of the active power p_a, that is used up to ionize the gases and for all chemical changes in the discharge region; *the energy efficiency* – the power factor gives an idea of the common power of the plasma generator working under the selected burning regime of the *LF-CD* discharge.

Our investigations on the *LF-CD* discharge allow to be defined any of the discharge burning regime varying one factor only – the voltage U_{eff} applied to the plasma generator. The selected U_{eff} values are suited in the two strongly distinguishing technological regimes of the plasma generator work, fig. 2c. The ammonia atmosphere is created through bring in of 10 ml 25 % water solution of ammonia per 100 g *WF* (with equilibrium humidity) in the closed volume of the plasma generator at atmosphere pressure – 0.1 MPa.

NR compounds, containing 50 phr *WF* (non-treated or ammonia plasma treated) were prepared on lab rolls in a conventional way. The vulcanization was carried out at a temperature of 170^{0}C for the optimum cure time estimated according to *BDS* 1573 - 83 with *Monsanto Rheometer*, model 100 S. The mechanical parameters were tested according to *ISO* / R37.

Results and Discussion

The screening investigation of *WF* filled rubber compounds demonstrates a sharp increase of the modulus M_{100} (up to about 3.5 times) and M_{200} (up to about 2.7 times) as compared to the non-filed control mixture. These changes are accompanied by significant decrease of the tensile strength, σ (down to about 4 times) and the elongation at break, ε (down to about 1.5 times).

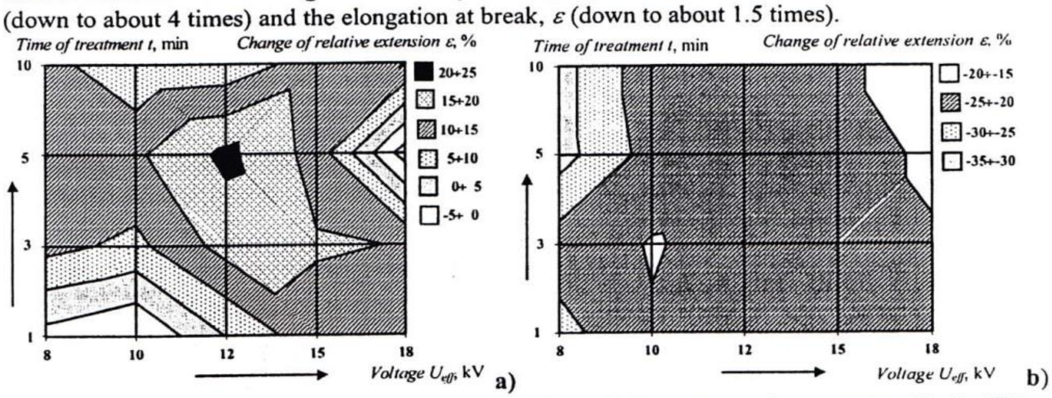
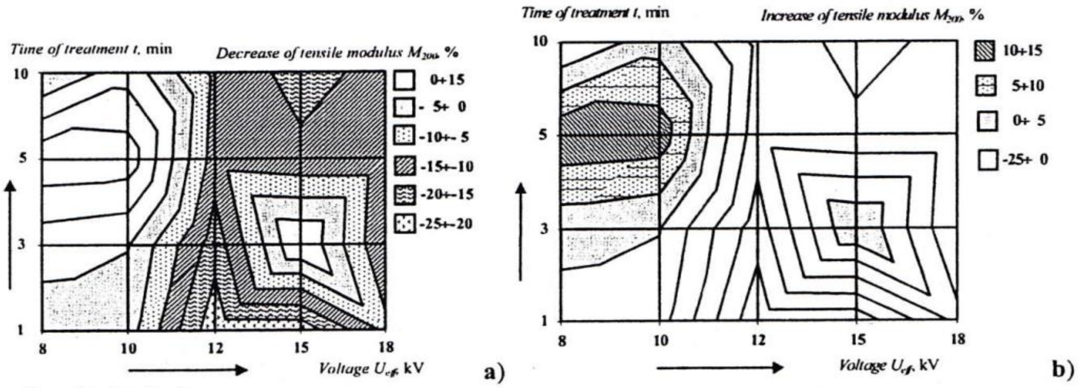


Fig. 4. Relative change of the elongation at break, ε of NR - compounds containing 50 phr WF treated in air (a) or ammonia (b) plasma obtained in LF-BD discharge. The relative change of the elongation ε at break is towards the elongation at break (ε = 410 %) of a control NR - compound filled with 50 phr non-treated WF. The elongation at break, ε of the control non-filled NR - compound was of 614 %.

Our plasma-chemical treatment was aimed at a saving of the high modulus of the *WF* filled *NR* - compounds and an improvement of the other mechanical parameters. It was found that the "dry" air plasma treatment leads to some improvement of the tensile strength σ and the elongation ε at break better expressed in the second, nitrogen regime – at 12 kV and more, fig. 3a and fig. 4a. This gives reason to be expected that the "wet" ammonia plasma treatment will be more effective in the *WF* surface modification regarding its reinforcing effect in *NR* - compounds. In the fig. 3 and fig. 4 are parallel given the results of the mechanical testing of *NR* - compounds filled by *WF* treated in air and ammonia plasma under both oxygen and nitrogen regimes. All results are presented as a relative change of the corresponding parameter toward its value for the control *NR* - compound filled by 50 phr non-treated *WF*.

The logic of our experiment is completely manifested at the change of the tensile strength, σ (see fig. 2 and fig. 3). Some think more, the maximal increase of the tensile strength is in region quite suitable from the technological point of view – the treatment time is of about 1 min at 15 kV.



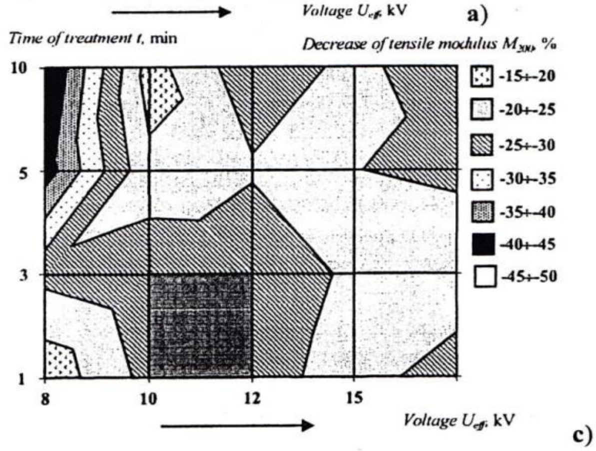


Fig. 5. Relative change of the modulus M_{200} of NR - compounds containing 50 phr WF treated in air (a, b) or ammonia (c) plasma obtained in LF-BD discharge. The relative change of the modulus is towards the modulus (M_{200} = 3.9 MPa) of a control NR compound filled with 50 phr non-treated WF. The modulus of the control non-filled NR - compound was of 1.5 MPa.

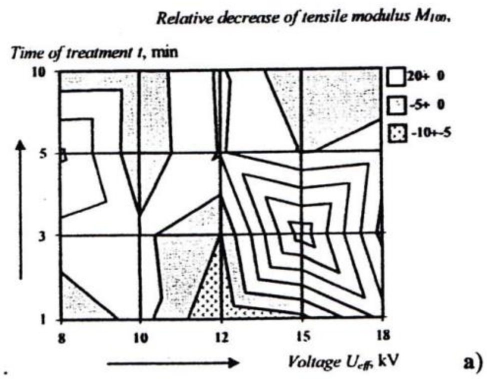
The change of the elongation at break, ε is opposite for the compounds filled with oxygen or nitrogen plasma treated *WF*, fig. 4. The plasma-chemical treatment of *WF* in oxygen plasma leads to an increase in the elongation ε at break of the filled *NR* - compounds whereas the treatment in nitrogen plasma decreases the same parameter with a similar percent.

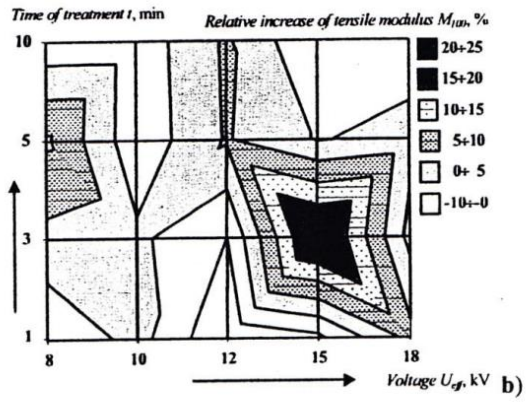
Different changes are observed also in the modulus of the studied rubber compounds depending on the plasma medium, fig. 5 and fig.6. Both modulus M_{100} and modulus M_{200} decrease (with 10÷20 % or 20÷30 % respectively) when the *WF* is treated in ammonia plasma, fig. 5c and fig. 6c. The change is opposite when the *WF* is treated in air plasma – modulus M_{100} and modulus M_{200} increase with about 25 % or 15 % respectively.

Conclusion

- *LF-BD* discharge is able to produce two types technological plasma at atmospheric pressure, depending on the operation conditions: ozone and oxygen containing one, generated at low voltages – under 10-12 kV and relative low density of active power – under 5 W/m^2 and nitrogen oxides and other active compounds containing plasma, generated at high voltages – over 12 kV and high surface density of active power – over 5 W/m^2;

- These two plasma regimes could be governed by the voltage and they get up "visible" thorough the experimental observed external static volt-ampere characteristic of *LF-BD* discharge from that come technology and energy current characteristics defining the plasma medium;
- The *WF* yields of plasma-chemical modification significantly better in the region of the "nitrogen" plasma of *LF-BD* discharge;
- The ammonia plasma reinforces the modification effect regarding some mechanical parameters of the *NR* - compounds filled by *LF-BD* discharge treated *WF*.





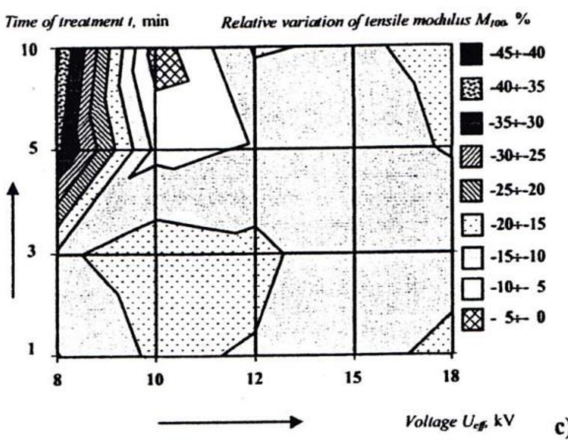


Fig. 6. Relative change of the modulus M_{100} of NR - compounds containing 50 phr WF treated in air (a, b) or ammonia (c) plasma obtained in LF-BD discharge. The relative change of the modulus is towards the modulus (M_{100} = 3.9 MPa) of a control NR - compound filled with 50 phr non-treated WF. The modulus of the control non-filled NR compound was of 1.5 MPa.

REFERENCES

1. P. Dineff. Electrotechnology. Part 1: Introduction in Electrotechnology. Sofia, Bulgaria, TUS, 2001 (in Bulgarian).
2. H. Katz, M. Milewski. Handbook of Fillers and Reinforcement for Plastics. Moscow, Chemie, 1981 (in Russian).
3. P. Dineff, D. Gospodinova. The surface density of the power as a basic parameter of the plasma-chemical modification of the materials in a barrier electrical discharge. - International conference ELMA' 02, September 13-14, 2002, Sofia, Proceedings, 2002, pp. 304-310.
4. P. Dineff, D. Gospodinova. Energy-effective plasma-chemical surface modification of polymers and polymeric materials at atmospheric pressure. - International conference MEDPOWER' 02, November 04-06, 2002, Athens, Proceedings, 2002, pp. 1124-1128.

ПРИЛОЖЕНИЕ:

Оригинални фигури – приложени са фигурите, които имат лошо качество и не могат да се ползват адекватно.

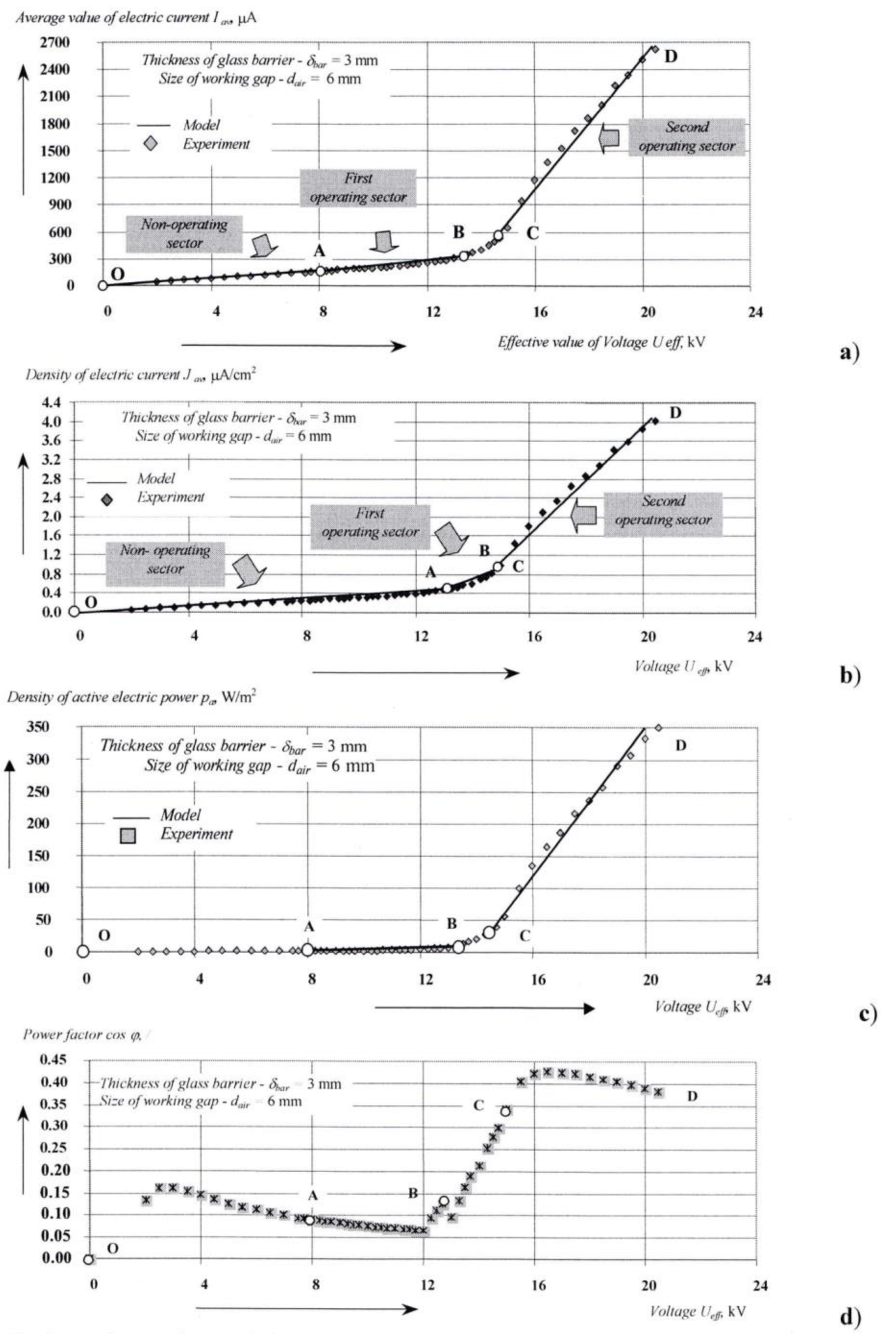


Figure 2. Operating regions of the external characteristic of low-frequency barrier discharge – the relationship between the average value of current I_{av} and the effective value of applied voltage U_{eff} (**a**):

OA – non-operating sector; *AB* – first operating sector, namely plasma containing ozone and products from its decomposition; *CD* - second operating sector, namely plasma containing nitrogen oxides; *BC* - transient region. Other electric characteristics of the discharge: current density J_{av} (**b**), surface density of active power p_a of the discharge (**c**) and the power factor $cos\ \varphi$ (**d**) as a function of the applied voltage U_{eff}.

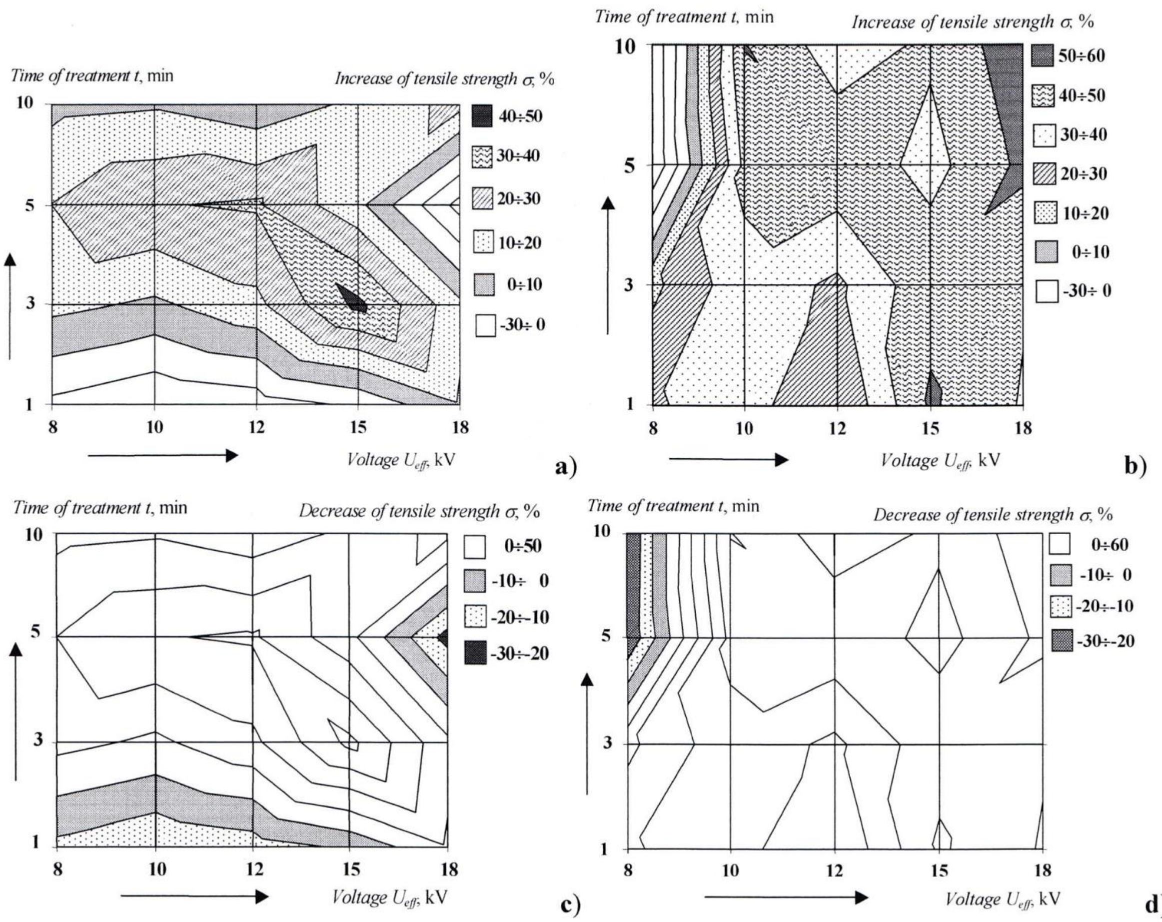


Figure 3. Relative change of the tensile strength, σ of *NR* - compounds containing 50 phr *WF* treated in air (**a, c**) or ammonia (**b, d**) plasma obtained in *LF-BD* discharge. The relative change of the tensile strength σ is towards the tensile strength (σ = **6.0** MPa) of a control *NR* - compound filled with 50 phr non-treated *WF*. The tensile strength of the control non-filled *NR* - compound was of **24.6** MPa.

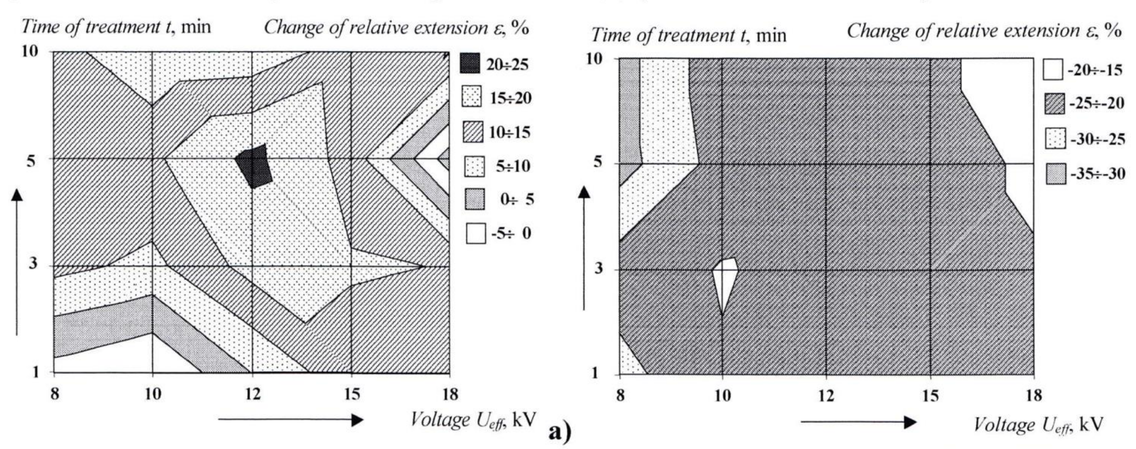
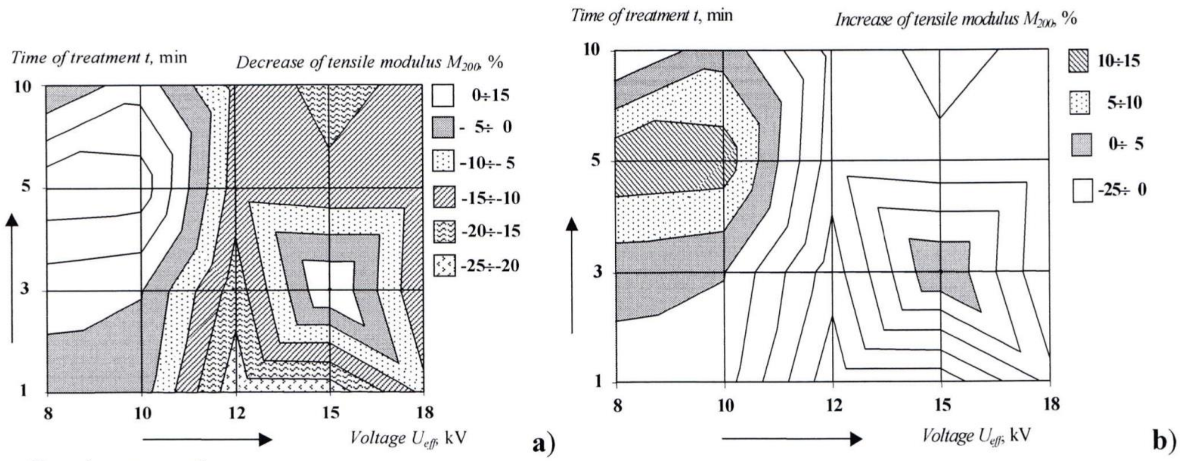


Figure 4. Relative change of the elongation at break, ε of *NR* - compounds containing 50 phr *WF* treated in air (**a**) or ammonia (**b**) plasma obtained in *LF-BD* discharge. The relative change of the elongation ε at break is towards the elongation at break (ε = **410** %) of a control *NR* - compound filled with 50 phr non-treated *WF*. The elongation at break, ε of the control non-filled *NR* - compound was of **614** %.



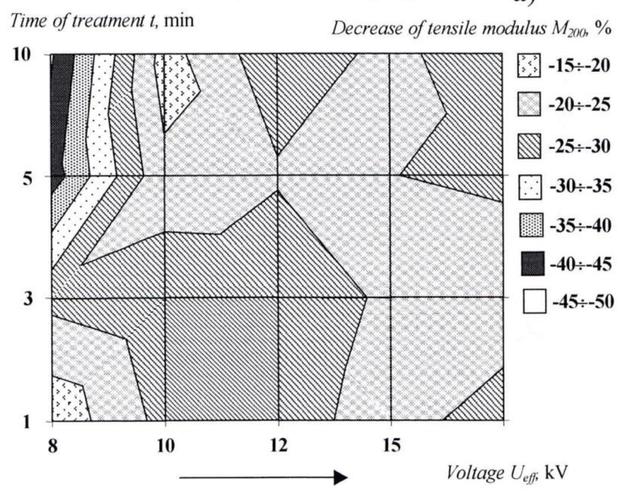
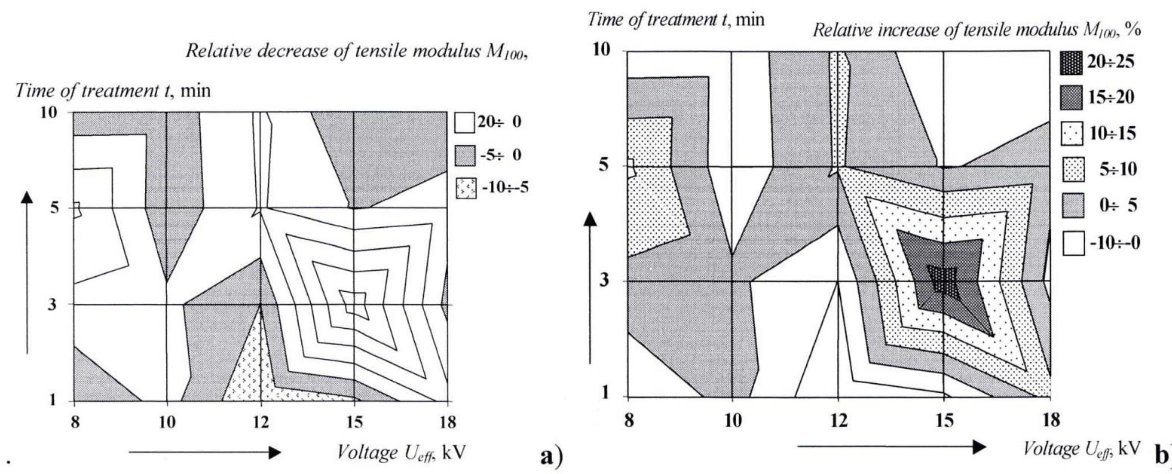


Figure 5. Relative change of the modulus M_{200} of *NR* - compounds containing 50 phr *WF* treated in air (**a**, **b**) or ammonia (**c**) plasma obtained in *LF-BD* discharge. The relative change of the modulus is towards the modulus (M_{200} = 3.9 MPa) of a control *NR* compound filled with 50 phr non-treated *WF*. The modulus of the control non-filled *NR* - compound was of **1.5** MPa.



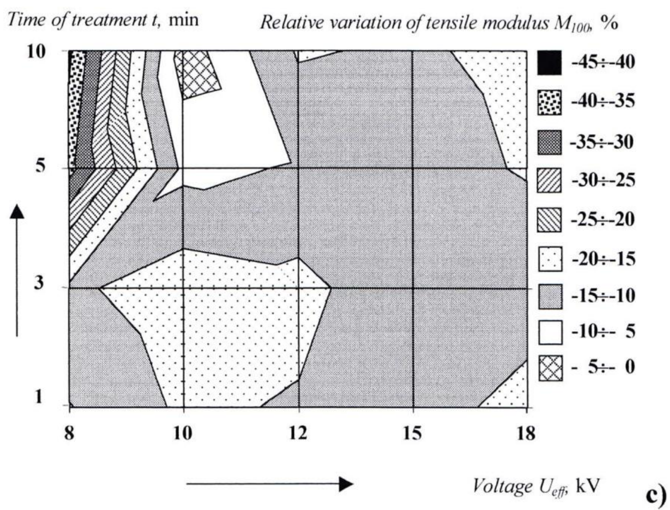


Figure 6. Relative change of the modulus M_{100} of *NR* - compounds containing 50 phr *WF* treated in air (**a**, **b**) or ammonia (**c**) plasma obtained in *LF-BD* discharge. The relative change of the modulus is towards the modulus (M_{100} = 3.9 MPa) of a control *NR* - compound filled with 50 phr non-treated *WF*. The modulus of the control non-filled *NR* compound was of 1.5 MPa.