RELAXATION EFFECTS IN DIELECTRIC SPECTRA OF OLIGOMER BUTADIENE MATERIALS

Salem El-Fakhri, Doctoral Degree Programme (2)
Dept. of Physics, FEEC, VUT
E-mail: xelfak00@stud.feec.vutbr.cz

Supervised by: Dr. Karel Liedermann

ABSTRACT

The object of this research is to measure and to analyze dielectric spectra of oligomer of butadiene. The analysis and subsequent interpretation is based first on detailed observation of temperature dependencies of the relaxation processes and second on the comparison of dielectric measurements made in different frequency ranges.

1 DIELECTRIC RELAXATION SPECTROSCOPY

It's necessary to select appropriate analytical method for research characteristics of materials. One of the modern experimental methods is the dielectric relaxation spectroscopy (DRS). In general, DRS studies molecular dynamics of current carriers, respectively dipoles and consist of a set of theories and methods used to experimentally research this dynamics. This research deals with the DRS of oligohydroxybutadiene. Surveyed sample is analyzed and evaluated in the frequency domain at different temperatures.

2 SAMPLE

The subject of experimental research and subsequent analysis of dielectric spectra has been hydroxyled oligobutadiene LBH, made in Kaucuk Kralupy Inc., which the producer sells with trademark KRASOL LBH. Oligobutadiene belongs to synthetic rubbers, which are matters containing dual bonds determining their characteristics.

There are two types of butadiene. The first one is KRASOL LB and polymer is fully linear and exhibits very narrow molecular weight distribution. Due to its low molecular weight, KRASOL LB is liquid at ambient temperature. It is manufactured in three grades KRASOL LB 2000, 3000 and 5000; numbers indicate the molecular weight. Typical chemical structure is as follows: **$H - (-CH_2\text{-}CH{=}CH\text{-}CH_2\text{-})_n - H$.**

The properties of KRASOL LBH are much the same as those of KRASOL LB; the main difference is that KRASOL LBH has terminal secondary hydroxyl groups.

2.1 PHYSICAL AND CHEMICAL CHARACTERISTICS

In the ordinary way, hydroxyled oligobutadiene is a clear, colorless till yellowish viscous liquid, that is non-miscible with water and alcohols. However it's well miscible with non-polar organic liquid, oils and pitches. Oligobutadiene is soluble easily in some different solvents and appertain to unsaturated alkaline hydrocarbons, which contain functional OH-group. It is produced by polymeric reaction.

2.2 APPLICATION

Liquid oligobutadiene KRASOL LBH is used for the production of polyurethane. Oligobutadiene polyurethanes are characteristic by their excellent hydrolysis resistance. These polyurethanes are also highly elastic, provide excellent insulating qualities for the electric current and leak very little moisture. Utilization of liquid oligobutadiene KRASOL LBH in practice is presented in [2].

3 EQUIPMENT FOR THE MEASUREMENTS IN THE FREQUENCY DOMAIN

Measurements in the frequency domain were carried out on the Hewlett Packard HP 4284A precision LCR meter and dielectric test fixture capacitor HP 16451B. Measuring with the precision LCR meter is based on bridge techniques with auto-calibration and its measured results are available over the frequency range 100 Hz - 1 MHz. It is necessary to carry out corrections before each measuring to avoid errors during the measuring. The sample was analyzed in the temperature chamber, which was for this experiment shown in Fig [1].

Fig. 1: *Equipments for the measurments in the frequency domain.*

4 EXPERIMENT EVALUATION

The characteristics e"=F(f) were measured and evaluated experimentally for the temperatures in the range from –20 °C to 20 °C.

The measurements might be interpreted as the evidence of the presence of at least one conductivity process left side and of a relaxation process rigth side. The left hand slope of the relaxation maximum i.e., the cooperation parameter α has the value of (0.48) which indicates a partially cooperative character of dipole motions. The relaxation process shifts from the high frequency side to the low frequency side and becomes unsymmetrical as the experimental temperatures decrease. The lack of symmetry might be due to the presence of either another relaxation process or conductivity which is seen at room temperature.

The analysis of experimental data has substantiated the appearance of relaxation processes in the sample of oligobutadiene. The relaxation maximums were moving towards lower frequencies with the decreasing temperature and that is why the relaxation maximums were perceptible. The rate of correlativity is the expressed the parameter α, that slightly decreases with the increasing temperature. It means that the orientation each of the molecules is less affected by others. Figure 2 shows (imaginary part of the complex permittivity).

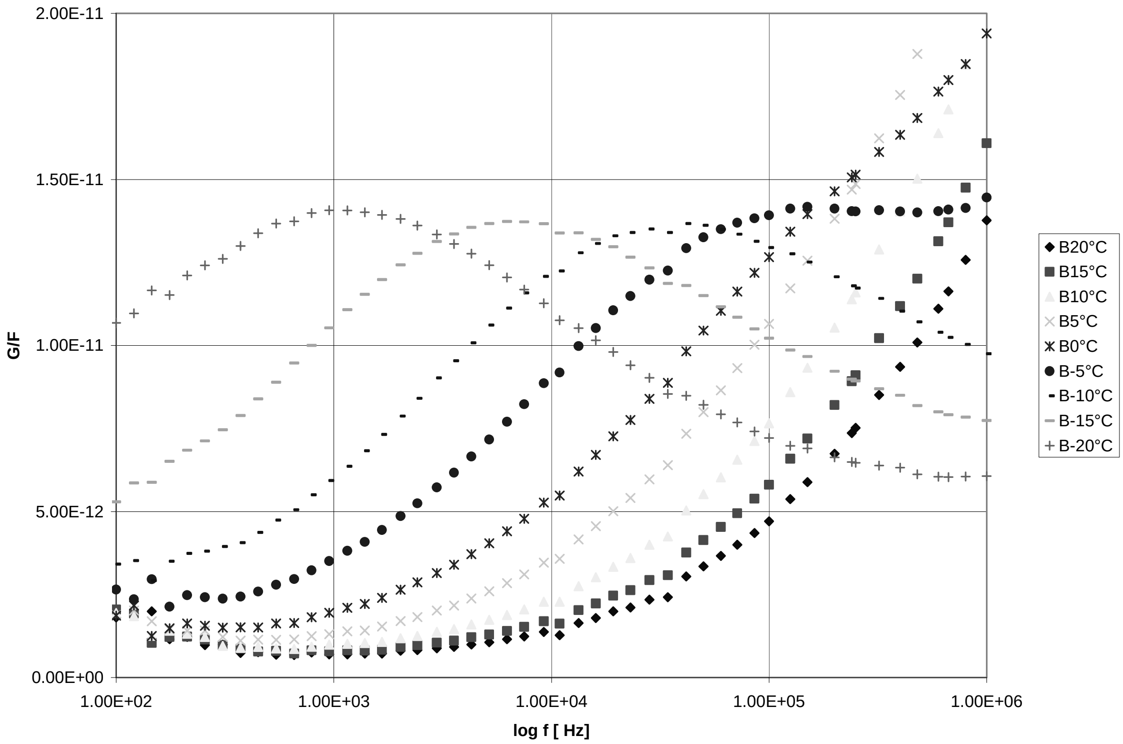

Fig. 2: *Relation between the G/F and log frequency*

5 CONCLUSIONS

Dielectric relaxation spectra of hydroxyled oligobutadiene LBH were measured in the frequency range from 100 Hz to 1 MHz and temperature range from 20 °C to -20 °C. The measurements might be interpreted as the evidence of the presence of at least one relaxation process right side, perhaps two at higher temperatures. The slope of the relaxation maximum at the room temperature (not shown here) has the value of (0.48) which indicates a partially cooperative character of dipole motions. The relaxation process shifts from the high frequency side to the low frequency side and becomes unsymmetrical as the experimental temperature decreases. The lack of symmetry might be due to the presence of either another relaxation process or conductivity which is seen at room temperature.

The type of relaxation mechanism corresponds with turning whole chain of hydroxyled oligobutadiene.

Experimental work with the oligobutadiene will be going on and the results will be published continuously.

ACKNOWLEDGEMENT

This paper is based in the research supported by the project MSM 1850031 and by the grant project No.102/03/621 provided by the Grant Agency of the Czech Republic. The support of the both projects is gratefully acknowledged.

REFERENCES

[1] Hedvig, P.: Applied Polymer Analysis and Characterization, Volume II, 1991, Hanser, New York.

[2] Oligobutadiene production manual. http//www.kaucuk.cz/

[3] Bottcher, C. J. F., Bordewijk, P.: Theory of Electric Polarization, Volume I: Dielectric in static fields, 1973, Elsevier, Now York

[4] Havriliak, S., Havriliak, S. J.: Dielectric and Mechanical Relaxation in Materials, 1997, New York