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MEASUREMENTS OF THE RAYLEIGH WAVE PROPAGATION VELOCITY IN THE POLYMER LAYERS

ZENOBIA KRZEŚNIAK, JERZY RANACHOWSKI, JADWIGA RZESZOTARSKA

Institute of Fundamental Technological Research Polish Academy of Sciences
(00-049 Warszawa, Świętokrzyska 21)

ZDZISŁAW JAKUBCZYK

Institute of Physics, Silesian Univ. of Technology
(44-100 Gliwice, Bolesława Krzywoustego 2)

In the paper are presented the results of measurements of the Rayleigh wave propagation velocity in the polyvinyl carbazole (PCV), polyvinyl carbazole with trinitrofluorenon (PVC-TNF) and their halogen derivatives. The correlation relationship between the activation energy of the investigated compounds and the linear combination of the squares of longitudinal and transverse ultrasonic wave velocity was found to be linear.

1. Introduction

The paper deals with the measurements of surface wave propagation velocity in the layers of PVC, PVC-TNF and their halogen derivatives.

Because of the interesting and promising properties of the polymers from the point of view of electronical applications, they are the object of interest of numerous scientific centres [2, 4, 9, 12, 13, 14]. Although a lot of information about polymers has been gathered, the trials to construct their theoretical model which would be capable of describing their experimentally observed electrical properties failed. Attempts are made of describing the mechanisms of carriers generation and transport in polymers with the models worked out for inorganic semiconductors. The assumption that lies in the basis of many such concepts, as the band or excitation model, is the existence of long range interactions. In numerous polymers which are amorphous or exhibit low level of crystallization the long range is found only in one direction. Nevertheless, the examples are known in which the band structure can be present in amorphic solids and where the exciton concept is also valid for polymers [13, 14]. It is understood that such application of notions which were introduced for crystalline materials is only the first approximation and it can not be applied without criticism. It is an experimentally verified fact that in semiconducting polymers the electron type, and not ionic type conduction takes place [12].

The phenomena, observed in polymers, concerned with the mechanisms of carrier generation and transport are similar to those observed in amorphous semiconductors [2, 3, 4] and perhaps will be described by the same relationships. Elaboration of a uniform model for polymers which would fully explain these phenomena is difficult for several reasons. Organic polymer semiconductors form a large group of materials. Most generally they can be divided into activated and nonactivated polymers, while further distinction can be made into optically activated (by adding a dye) and chemically activated (by forming donor-acceptor complexes also named charge-transfer complexes) [13]. Experimental data obtained by various authors differ what is probably caused by technologically different preparation of samples. As it has been found, not only the chemical modification impurities or structural defects influence the result, but also physical conditions (e.g. atmospheric conditions) during the preparation of samples and measurements [12, 4].

In spite of the above mentioned significant influence of many factors on the results of electrical experiments on polymers, decision has been made to introduce acoustic methods into the investigations of electrical properties of these materials. An encouraging circumstance was that in the case of inorganic semiconductors in which an electron type conduction is observed a linear relationship occurs between the energetic gap width and the acoustic field parameters [5, 11]. The aim of the present paper is an attempt to find out if similar relationship hold for inorganic semiconductors. The experimental investigations indicated that such linear correlation relationship exists for the tested polymers.

2. Experiment

2.1. *Measurement samples*

Experiments were carried out on polyvinyl carbazole (PVC) – Fig. 1 and its compounds. The halogen derivatives of PVC were obtained with two methods. The first method was to introduce a halogen to the monomer ring and then to polymerize it. The second consisted in introducing a substituent to the PVC available in the market. The substitution reaction and the radical polimerization was carried out in solutions. The 1:1 molar ratio charge transfer complexes (CT) were obtained by mixing the equimolar volumes of the solutions of the donor (PVC and it's halogen derivatives) and the acceptor (trinitrofluorenon TNF).

Acoustical methods gained a number of applications in testing of the properties of media, with the use of these methods also the electrical properties correlated with

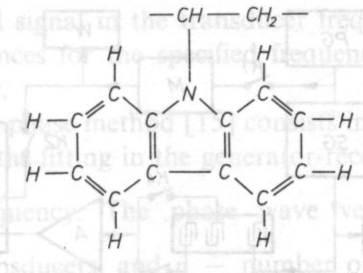

Fig. 1. Chemical formula of the polyvinyl carbazole PVC

the elastic waves propagation constants were investigated [1]. The condition for using the volumetric wave in the experiments is obtaining the samples of dimensions 15mm × 5mm × 5mm, adequately homogeneous and free from porosity and cracks. This condition turned out to be unsatisfiable, because the samples were obtained by pouring out the solution of the compound and letting the solver evaporate slowly. Hence the necessity arose to restrict the measurements to thin layers and to apply the surface waves in the tests [1, 8].

Accounting for the fact that the investigated polymers (PVC compounds) do not exhibit piezoelectric properties, it has been necessary to choose the substrate in which generation, propagation and receiving surface waves would be possible. The quartz slabs of Y cut have been applied. The system of transducers was formed with the photolithographical method. Nine interdigital transducers were used (three for each frequency), which generated the surface waves of basic frequencies: 27 MHz, 52 MHz and 63 MHz. The polymer layer was poured out on the substrate prepared in this way. After measuring surface wave velocity for a given layer thickness the next layer was applied. Every time the polymer was applied and the solver evaporated, the assembly was held at a temperature of about 423 K to remove the solver. Thicknesses of the layers ranged between 1 μm and 25 μm.

2.2. *Measuring technique*

Rayleigh wave propagation velocity in the samples was measured with the following methods:

- pulse method,
- phase-interference method,
- zero phase method.

Measurement of using pulse method allows for measuring group velocity. The block diagram of the measuring set has been displayed in Fig. 2. The value of the surface wave velocity has been calculated as a ratio of distance and pulse propagation time between transducers. The time was found by comparison with the period of a rectangular pulse generator. The distance between transducers was measured with the toolroom microscope, with the accuracy of ± 1μm.

The phase interference method [6, 15] consists in measuring the frequencies of

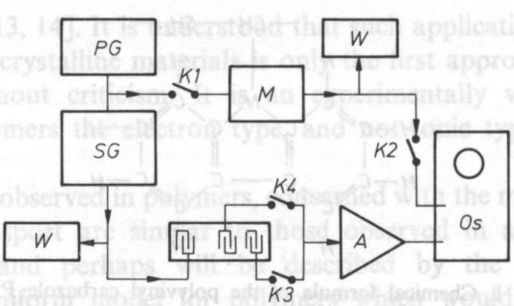

Fig. 2. The block of the measuring set. *SG* — signal generator, *PG* — pulse generator, *M* — modulator, *W* — wavemeter, *A* — amplifier, *Os* — oscilloscope

phase coincidencies in the transmitted frequency band of the interdigital transducers. The frequency band of a symmetrical interdigital transducer is:

$$\Delta f = \frac{f_0}{N_0},$$

where N_0 — number of pairs of electrodes, f_0 — resonance frequency. The highest frequency of the band equals

$$f_g = f_0 + \frac{\Delta f}{2} = f_0 \frac{2N_0+1}{2N_0},$$

If the distance between the centres of the transducers is L, then at resonance the number of wave lengths fitting into this distance is $L/\lambda_m = m_0$. The lowest frequency of the band will be:

$$m_0 + \Delta m = \frac{L}{\lambda_0} + \Delta m.$$

Wave length for this frequency equals:

$$\lambda = \frac{L}{m_0 + \Delta m} = \frac{V_f}{f_g} \frac{2N_0}{2N_0+1}.$$

After elementary transformations we obtain:

$$\Delta m = \frac{L}{2N_0 \cdot \lambda_0}.$$

Because $N_0\lambda_0$ is the transducer width, and under the assumption that L is equal to the doubled width, we have $\Delta m = 1$.

Generally speaking, if

$$N < \Delta m < N+1$$

where N is a natural number, then there can be $2N+1$ phase coincidence between the generated and received signal in the transducer frequency band. Knowing the number of phase coincidences for the specified frequency, we can find the phase velocity for this frequency.

The concept of the zero phase method [15] consists in finding the changes of the complete surface wavelengths fitting in the generator-receiver distance for changing the excitation signal frequency. The phase wave velocity is $v = \frac{L\Delta f}{nL}$, where L – distance between transducers, and n – number of phase changes by 2π for frequency change of Δf.

2.3. Results of the measurements and their discussion

The investigated layer system consists of two materials with different elastic properties; therefore the velocity dispersion phenomenon takes place in this system. For a change in wave frequency or layer thickness the phase and group velocity changes can be observed then. From the theory of layer systems [1, 14] it follows that of the layer „loads" the substrate, i.e. if the elasticity coefficients of the layer are smaller than those of the substrate, then for growing frequency f and layer thickness h the value of the surface wave velocity v_R decreases from its value in the substrate to the value in the layer. It follows from the fact that the acoustic surface wave is a wave which vanishes in the distance of several wave lengths from the free surface of the material in which it propagates. If the layer is thick enough, the major part of the acoustic field energy is transmitted by the layer, which then determines the properties of the field.

The phase and group velocity dispersion has been measured for the two first modes of a surface wave for six polymer compounds (PVC and it's derivatives). The results are shown in the Table 1.

Table 1. Acoustic wave velocities for the investigated compounds [11]

Compound	C_R [m/s]	C_t	C_l
PVK	2600	2810	5135
PVK-Br_2	2890	3120	5763
PVK-Cl_2	2850	3065	5906
PVK-TNF	2535	2890	4120
PVKBr_2-TNF	2730	3020	4746
PVKCl_2-TNF	2645	2900	4767

The example dispersion characteristic for the first mode of the surface wave for a PVC-TNF compound is shown in Fig. 3.

It is known from the literature [1, 8] that in the case where the layer „loads" the

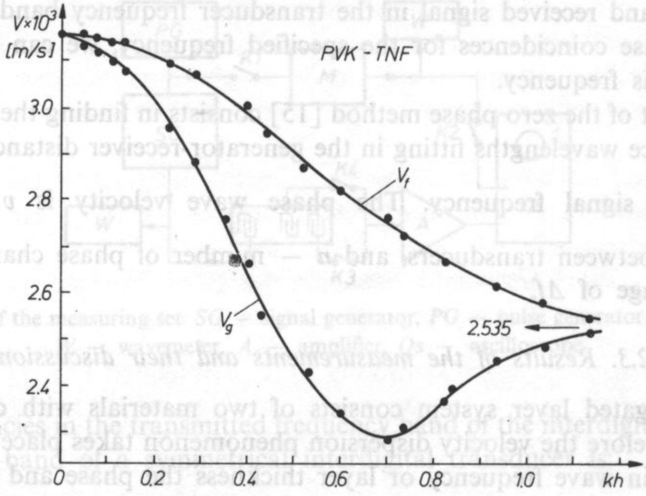

Fig. 3. Dispersion characteristic of the tested layer systems

substrate, for $kh \to \infty \left(k = \frac{2\pi f}{v_R} \right)$ the velocity of higher order modes of the surface wave tends asymptotically to the transverse wave velocity in the material of the layer. Furthermore it is known that together with the frequency growth, the displacement amplitudes of particles vanish slower for higher modes, what for the given layer thickness gives slower decay of the amplitudes of signals resulting from these modes. This makes it possible to measure the dispersion of higher modes for large layer thicknesses and to measure the transverse wave velocity for the materials of layers.

If the Rayleigh wave velocity v_R and transverse wave velocity v_t is known for the given compound, the logitudinal wave velocity v_l can be found from the known Rayleigh formula

$$\left[2-\left(\frac{V_R}{V_t}\right)^2\right]^2 = 4\left[1-\left(\frac{V_R}{V_1}\right)^2\right]^{1/2}\left[1-\left(\frac{V_R}{V_t}\right)^2\right]^{1/2}.$$

The velocity values found for the compounds under investigation are listed in the last column of Table 1.

In the papers [5, 10] it has been demonstrated that exists a relation between the width of the energetic gap E_g and the ultrasound wave velocity in the inorganic semiconductors of various types. Such relation has also been demonstrated for the conducting glasses. In the case of inorganic semiconductors the linear relation between the energetic gap width and the linear combination of the squares of propagation velocities has been obtained for the compounds having one type of bondings [10].

Conducting polymers characterize themselves by a far more complex structure and more diverse conduction mechanisms. The electrical properties of the investiga-

Table 2. Activation energies of the investigated compounds [7]

Compound	Voltage [V]	Activation energy [eV]
PVK	50	0.2
PVK-TNF	50	0.66 ± 0.04 0.17 ± 0.06
$PVKBr_2$-TNF	50	0.92 ± 0.04 0.31 ± 0.06
$PVKCl_2$-TNF	50	0.64 ± 0.05 0.63 ± 0.05
$PVKBr_2$	50	0.32 0.2
$PVKCl_2$	50	0.65 0.12

ted compounds have been presented in the paper [7]. The common feature of the majority of polymers is the activated character of conduction. This is concerned with the necessity of providing sufficient energy for releasing the charge carrying complex. On the basis of the results of activation energy measurements with the use of electrical methods [7] (Table 2) and ultrasonic waves propagation velocity, it has been demonstrated that there exists a linear correlation relationship between the activation energy and the propagation velocity for the investigated group of polymers (Fig. 4), similarly as in the case of inorganic semiconductors [5, 10].

The inorganic compounds exhibited the electron type conduction. It has been stated then, that the compounds of similar ionity of bondings formed straight lines in the plane $(V_L^2 - 4/3\,V_t^2) \times 10^6\,[\mathrm{m}^2/\mathrm{s}^2]$, E_g while the compounds with different bonding ionity formed different lines. Nevertheless, the type of the relation was always linear. As it has been mentioned previously, the above described polymer

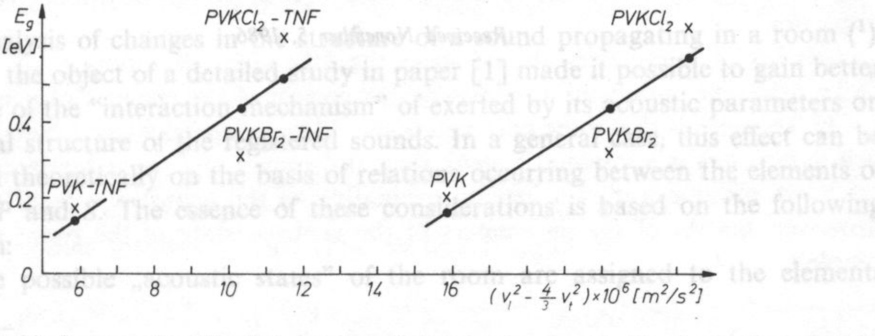

Fig. 4. Relationship between the activation energy and ultrasound wave velocities for the investigated compounds. The mapping of the abscissa into the ordinate shown in the figure with the three points has been linearly approximated with the least squares method

compounds have had the similar properties: PVC and it's halogen derivatives form one straight line in the plane $(V_l^2 - 4/3 V_t^2) \times 10^6 [\mathrm{m}^2/\mathrm{s}^2]$, E_g while the PVC-TNF and it's halogen derivatives form another line.

The question arises, if a conclusion about the electron type conduction in the investigated polymers made on the basis of the observed linear correlation relationships is justified, similarly to the case of inorganic semiconductors. The presented results do not allow to answer this question in a unique way, without carrying out some further studies.

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