Configuration Transformations in Polyvinyl Chloride−Methylene Blue Composites

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Bulk samples of pure polyvinyl chloride (PVC) and its composites with different content of methylene blue (MB) dye are prepared. The degree of crystallinity, dynamic elastic modulus E and shear modulus G (~ 1 MHz), photoluminescence (PL), temperature dependences of dielectric characteristics ε_1, ε_2, tgδ, electrical resistance R at different frequencies of alternating electric field are measured. As shown, the adding of a modifier (MB) with conjugated chromophores is accompanied by both the generation of linear conjugated systems (polyenes) in PVC and the destruction of monomer units. These processes are mechanisms for changing the mechanical, structural, optical, dielectric properties of PVC−MB composites caused by the peculiarities of the stack interaction between their conjugated components.

Виготовлено об'ємні зразки чистого полівінілхлориду (ПВХ) і його композитів з різним вмістом барвника метиленового синього (МС). Проведено міряння ступеня кристалічности, динамічних модулів пружности E і зсуву G (~ 1 МГц), фотолюмінесценції (ФЛ), температурних залежностей діелектричних характеристик ε_1, ε_2, tgδ, електроопору R за різних частот змінного електричного поля. Показано, що внесення модифікатора (МС) із спряженими хромофорами супроводжується ґенерацією у ПВХ лінійних спряжених систем (полієнів) і деструкцією мономерних ланок. Вказані процеси є механізмами зміни механічних, структурних, оптичних, діелектричних властивостей композитів ПВХ−МС, викликаних особливостями стекової взаємодії між їхніми спряженими компонентами.

Key words: polyvinyl chloride, methylene blue, conjugated systems, polyenes, dynamic moduli, photoluminescence, dielectric characteristics.

1. INTRODUCTION

Improving the properties of polymers in many cases is achieved by the introduction of various fillers, among which the most important are metal particles and carbon nanostructures [1, 2]. Particle distribution and their adsorption characteristics play an important role in the filling of polymer matrices. For magnetic fillers, it is important to be able to influence this distribution by an external magnetic field, which can be used to reduce, for example, the percolation threshold [3, 4]. Given the high aspect ratio for carbon nanostructures and the peculiarities of their segregated distribution, it is possible to obtain extremely low values of the percolation threshold, while maintaining a significant increase in electrical conductivity [5, 6]. If polymers are filled with carbon nanotubes, a significant increase in thermal conductivity is also achieved [7, 8]. However, the increase in the transport characteristics of polymers is significantly limited by the presence of high contact resistance between the components of the composites, and its overcoming has been insufficiently studied. There are methods of its suppression by introducing modifiers into the polymer matrix in the form of ionic salts [9–11] or conjugated systems [12–17]. It is possible to expect improvement of properties of matrices filled with the conjugated modifiers, first, for polymeric chains, in which links π-conjugated sites take place too. In this case, we can expect the emergence of stack interaction between the components of composites and, as a consequence, the improvement of their properties [15].

At the same time, there are polymers, such as polyvinyl chloride, in which conjugated systems in the form of polyenes with different numbers of π-conjugated units are formed quite easily because of dehydrochlorination [16–18].

The generation of polyene structures in PVC can be stimulated by modifying the PVC matrix with fillers, in the molecular structure of which there are conjugated links. The number and type of polyene structures in PVC will be dependent on the content of the modifier with a conjugated structure. Since stack interaction can be expected between the modifier and the generated polyenes, this can lead to a change in the electrically conductive, thermally conductive, mechanical, and optical properties.

In addition, when introducing conductive fillers into the polymer

matrix by reducing the contact resistance of the modified polymer matrix, changes in the formation of percolation clusters and, therefore, improvement of the transport properties of polymer composites are possible.

The purpose of this work is to study the formation of polyene structures in the polymer matrix of polyvinyl chloride in the creation of PVC composites with molecules of methylene blue (MB), including conjugated systems.

2. EXPERIMENTAL

Composites of polyvinyl chloride C-7058 ($M_w = 157 \cdot 10^3$, Ukraine) with methylene blue (MB) dye were obtained by hot compression method. The temperature of preparation is of 120–130°C. Molecular formula of MB is $C_{16}H_{18}ClN_3S$; its molecular weight is of 319.85 g/mol. The obtained PVC–MB composites were as discs with a diameter of 30 mm. The concentrations of MB in the polymer matrix were 0–0.07 vol. fract.

The mechanical properties of nanocomposites PVC–MB by the ultrasonic KERN-4 (Ukraine) computerized velocity meter were investigated [19].

The PL spectra of pure PVC and PVC–MB composites were measured at room temperature with the Horiba Jobin Yvon T64000 triple spectrometer (Japan). The spectra were excited by He–Cd laser with the wavelength $\lambda_L = 325$ nm.

The dielectric investigation was performed by the thermostatted four-electrode cell method. ε', ε'', tgδ and R were measured at four frequencies $f = 5$, 10, 20, 50 kHz, within the temperature range of –50–50°C. An automated setup based on the alternating-current bridge P5083 was used [20].

3. RESULTS AND DISCUSSION

Polyvinyl chloride (PVC) is the polymer with a low content of crystalline phase. If PVC is filled with MB dye, with increasing concentration of the modifier, the degree of crystallinity, dynamic elastic modulus and shear modulus are changed in a complex way (Fig. 1).

It is seen that, at low concentrations of MB, the degree of crystallinity increases sharply and there is a maximum at MB concentration of about 0.01 vol. fract. Dynamic modules are also growing at low MB content. At higher concentrations of dye, there are a wide maximum and a minimum at about 0.05 vol. fract. for both dynamic moduli E' and G'. As the content of MB increases, these modules are increasing.
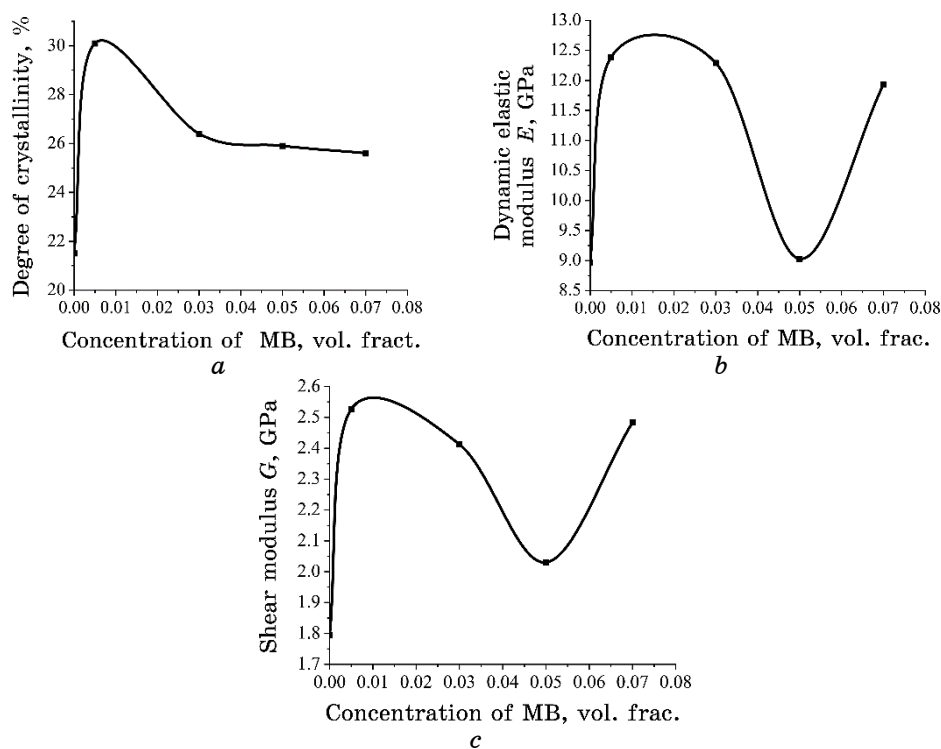
Fig. 1. Dependence of the degree of crystallinity (*a*), dynamic elastic modulus (*b*) and dynamic shear modulus (*c*) for the PVC–MB composites.

Since the values of the dynamic modules were determined from the travel speeds in the samples of PVC and its composites at high sound frequencies (~ MHz), they are associated with conformational changes of the monomer units. These changes are limited by the height of the potential barrier that arises due to the available intramolecular inhibition forces of rotation of these units. Obviously, the complex behaviour of both dynamic modules is due to the changes in the height of this barrier with increasing of MB content in the vitreous state of the polymer. The change in the height of the braking barrier is primarily associated with the rearrangement of the molecular structure of the monomer units and the destruction of the PVC macromolecular chain. Such destruction of PVC can be caused by dehydrochlorination with simultaneous generation of polyene structures [21, 22]. Since the modifier promotes the formation of a crystalline phase in PVC, the considered dehydrochlorination may be as consequence of the emergence of supramolecular structures. The generation of polyene systems, as the installation of new configurations of monomer units in the presence of double
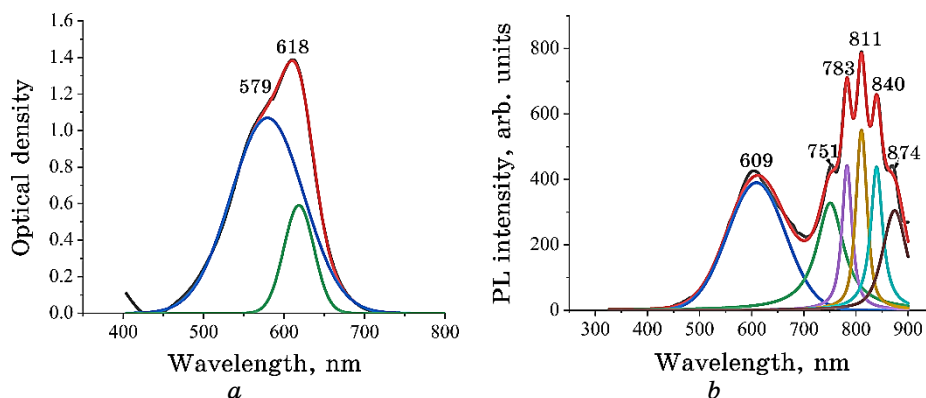
Fig. 2. Optical density (*a*) and photoluminescence spectra (*b*) for MB; $\lambda_{ex} = 325$ nm, $T = 298$ K.

bonds in them, provides the increasing in the dynamic modules associated with the relaxation of these units.

Figure 2 presents the spectra of optical density (OD) and photoluminescence (PL) for MB.

The OD and PL spectra of methylene blue reflect the electronic transitions due to the complex system of energy states inherent in the MO of π-electrons, which are characteristic of MB [23].

As seen, in the emission spectrum, in addition to the maximum at about 609 nm, there are several intense PL peaks concentrated in the near-IR region.

Figure 3 shows the PL spectra for pure PVC and its composites with different MB content. It is seen that the PL of conjugated structures of PVC and MB are significantly different. If, for PVC after the transfer of excitation energy from the carbonyl group, there are emission maxima from several types of conjugated systems at 472, 535, 586 nm, as well as from individual conjugated functional groups in the IR region, the PL for MB in the presence of one of the peaks around 609 nm are concentrated in the IR-wavelength range. The intensity of the bands at 751, 783, 811, 840, 874 nm exceeds its value for the band at 609 nm. In the PVC–MB composites, weak peaks in the IR region persist. At the same time, even with a small content of modifier (0.005 vol. fract. MB), there is a significant rearrangement of the PL spectrum of the composite, compared with pure PVC. First, the intensity of PL increases by several times. The position of the main emission maximum is shifted to 564 nm. In addition, there is a high-intensity band around 694 nm. This rearrangement of the spectrum indicates significant transformations of the polyene structures, which are in the PVC polymer matrix. Polyene systems are becoming more homogeneous,
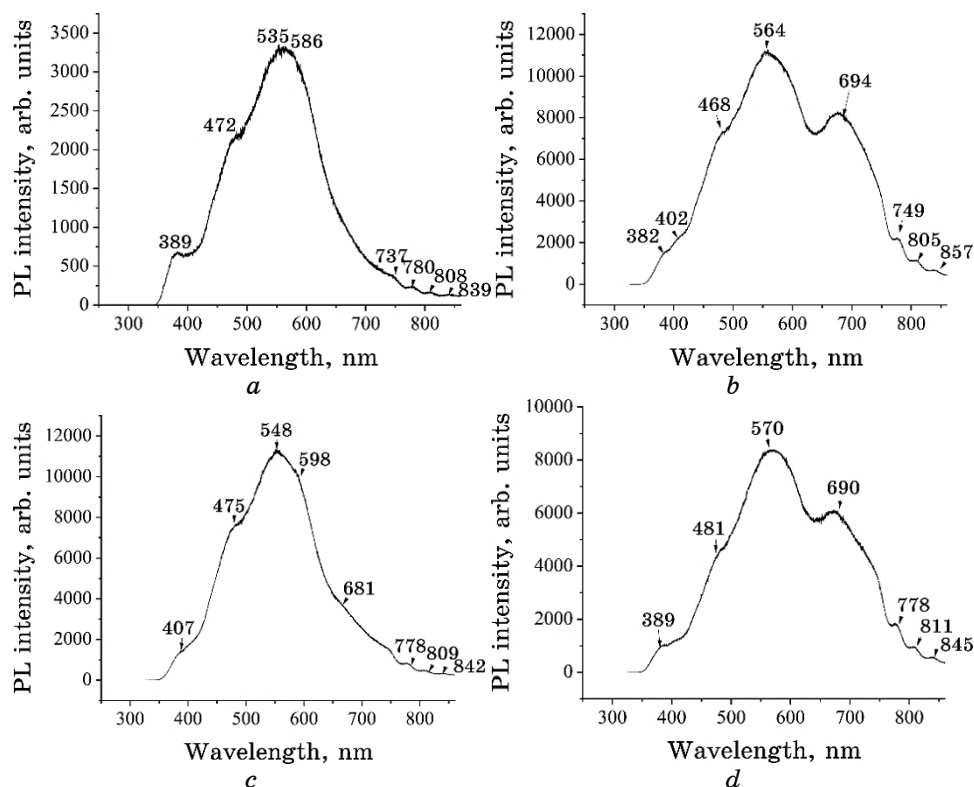
Fig. 3. PL spectra of pure PVC (*a*) and PVC–MB composites with 0.005 (*b*), 0.03 (*c*), 0.05 (*d*) vol. fract. MB ($\lambda_{ex} = 325$ nm, $T = 298$ K). The thin lines are corresponding to the spectra components.

their number is constantly growing. But there is an additional type of longer polyene chains, the PL peak, located at about 694 nm.

In the PVC composite with 0.003 vol. fract. MB, the general trend of increasing the number of polyenes persists, but there is a restructuring in the polyene system, because, to replace the peak at about 694 nm, there are inflections in the PL band due to the appearance of additional polyene structures. This rearrangement is determined not only by the formation of polyenes responsible for the conjugation of MB, but it is also consequence of the destruction of monomeric PVC units during their stack interaction with the conjugated MB system. The result of such destruction is a noticeable drop in the intensity of the PL band, which corresponds to the polyene structures in the composite, when the MB content increases to 0.05 vol. fract. At the same time, the PL spectrum for this composite becomes similar to the PL spectrum of the composite with 0.005 vol. fract. MB.

PVC belongs to the polar plastics, and, in their structure, there is an inhomogeneous distribution of electrons that leads to a significant dipole moment. The presence of such a moment determines the dielectric properties of PVC, including the dielectric constant ε_1 (real component of ε), dielectric loss ε_2 (imaginary component of ε), loss factor tgδ. These dielectric characteristics, due to relaxation processes, depend on the frequency of the external electric field and temperature.

The molecular structure of the MB dye also leads to its polarity. Doping of the polymer matrix with polar fillers, in this case with MB, is accompanied by changes in the properties of polymers [24, 25]. The real component of the dielectric constant of pure PVC (ε) ε_1 increases with increasing temperature (Fig. 4). The dielectric constant increases similarly with temperature. At the same time, wide bands appear at the inflection positions of ε_1, which are better manifested at lower electric-field frequencies. These bands also occur on the curves of the temperature dependence of the dielectric-loss fac-
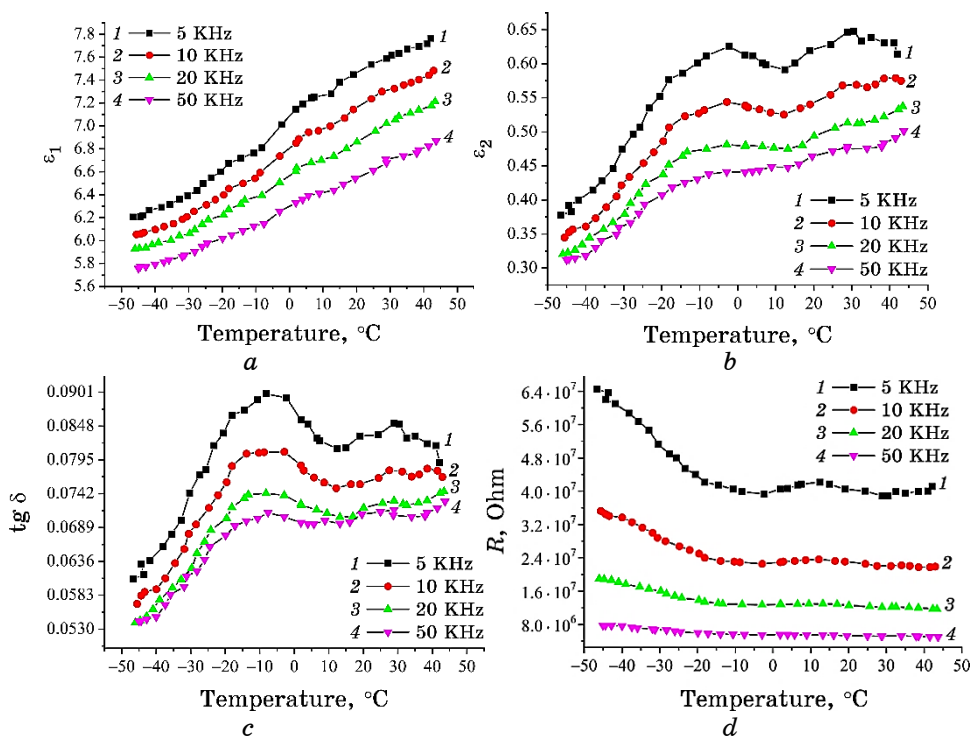

Fig. 4. Temperature dependences of dielectric characteristics ε_1 (*a*), ε_2 (*b*), tgδ (*c*), and electrical resistance $R(d)$ for pure PVC at different frequencies of alternating electric field.

tor tgδ and electrical resistance. At lower temperatures, the electrical resistance increases sharply. These behavioural properties of dielectric properties and electrical resistance are due to the relaxation of functional groups of PVC monomer units, which affect the pliability of electric dipoles existing in this polar polymer to orient along the alternating voltage of the applied electric field.

The doping of PVC with conjugated MB molecules leads to a change in the temperature–frequency dependences of ε_1, ε_2, tgδ and R. These changes are manifested even at low MB content (0.005 vol. fract.) and amplified at a dye concentration of 0.03 vol. fract. The trend of these changes is maintained for the PVC–MB composite with a content of conjugated modifier of 0.05 vol. fract. (Fig. 5).

It should be noted that the nature of the general changes in these parameters with temperature and electric field frequency is preserved. The values of ε_1, ε_2, tgδ increase with increasing temperature, and the electrical resistance R decreases. With increasing frequency of the electric field, for pure PVC and its composites, all the
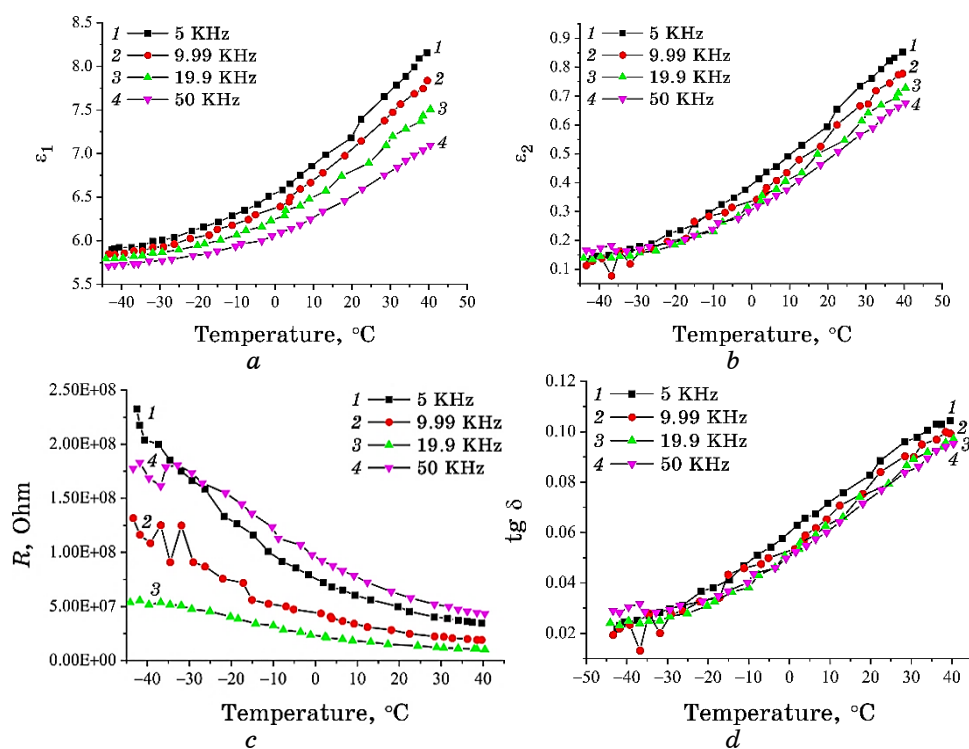

Fig. 5. Temperature dependences of dielectric characteristics ε_1 (*a*), ε_2 (*b*), tgδ (*c*), and electrical resistance R (*d*) for the composite of PVC with 0.05 vol. fract. MB at different frequencies of alternating electric field.

considered values decrease. At the same time, the behaviour of the considered dependences, the values of the parameters are significantly changed. First, there is a decrease in the values of ε_1, ε_2, tgδ and an increase in the electrical resistance R. If, for pure PVC, there is the noticeable frequency dependence, then, for composites, it is more pronounced only for high temperatures. The strips of relaxation processes, the presence of which is clearly visible for PVC, are absent. This behaviour of the considered dependences indicates the degradation of the molecular structure of PVC, primarily the functional group C–Cl, responsible for the polymer polarization.

4. CONCLUSIONS

In PVC composites with MB dye, the complex transformations of the degree of crystallinity, dynamic moduli of elasticity and shear occur, when the MB content changes.

The studies of PL spectra for PVC composites with different concentrations of MB indicate a significant rearrangement of polyene structures formed with the addition of the modifier. This rearrangement of the spectra indicates the destruction of the monomeric units of PVC and the generation of additional conjugated systems in the polymer. In this case, several types of polyene structures appear in composites with different lengths of π-conjugation that is accompanied by the appearance of several separate components in the PL band.

The destruction of PVC and the emergence of polyene structures lead to changes in the polarity of monomer units in PVC–MB composites and, as a consequence, to changes in temperature dependences of dielectric characteristics ε_1, ε_2, tgδ and electrical resistance R in comparison with their behaviour for pure PVC that confirms assumptions about configuration transformations in PVC due to the introduction of the MB modifier.

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