Mechanisms for increasing dynamic moduli in low density polyethylene composites with methylene blue dye

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The crystalline structure, degree of crystallinity, dynamic modules, Raman photoluminescence were studied for low-density polyethylene composites with different content methylene blue dye. It is shown that the degree of crystallinity varies little in a wide range of the modifier content (0−0.07 volume fraction). There is a non-monotonic concentration dependence of the elasticity modulus, shear modulus and Poisson coefficient; this indicates the formation of polymer layers on the dye surface, which are responsible for improving the physical and mechanical properties of the composite. In the immobilized layers, the intermediate phase of the polymer with oriented chains occurs, the conformation of which changes with an increase in the dye content. This phase is characterized by a complex defective structure, including polyene units of different lengths.

Keywords: low density polyethylene, dye, elastic modulus, shear modulus, crystallinity, polyene structures.

Механізми підвищення динамічних модулей у композитах поліетилену низької густини з барвником метиленового синього. *М.А.Александров, Т.М.Пінчук-Ругаль, О.П.Дмитренко, М.П.Куліш, Ю.Є.Грабовський, А.П.Онанко, А.І.Місюра, О.Л.Павленко, А.І.Лесюк, І.П.Пундик, Т.О.Буско, В.В.Стрельчук, О.Ф.Коломис.*

Вивчено кристалічну структуру, ступінь кристалічності, динамічні модулі, комбінаційне розсіяння світла, фотолюмінесценцію композитів поліетилену низької густини з барвником метиленовим синім за різного вмісту присадок. Показано, що у широких межах вмісту модифікатора (0−0,07 об. част.) ступінь кристалічності змінюється мало. Спостерігається немонотонна концентраційна залежність модулей пружності, зсуву, коефіцієнта Пуассона, яка свідчить про формування шарів полімеру на поверхні барвника, що відповідають за покращення фізико-механічних властивостей композиту. В іммобілізованих шарах відбувається зародження проміжної фази полімеру з орієнтованими ланцюгами, конформація яких змінюється при зростанні вмісту барвника. Дана фаза характеризується складною дефектною структурою, що включає полієнові ланки різної довжини.

Изучена кристаллическая структура, степень кристалличности, динамические модули, комбинационное рассеяние света, фотолюминесценция композитов полиэтилена низкой плотности с красителем метиленовым синим с различным содержанием присадок. Показано, что в широких пределах содержания модификатора (0−0,07 об. част.)

степень кристалличности изменяется мало. Наблюдается немонотонная концентрационная зависимость модулей упругости, сдвига, коэффициента Пуассона, которая свидетельствует о формировании слоев полимера на поверхности красителя, отвечающих за улучшение физико-механических свойств композита. В иммобилизованных слоях происходит зарождение промежуточной фазы полимера с ориентированными цепями, конформация которых сменяется при росте содержания красителя. Данная фаза характеризуется сложной дефектной структурой, включающей полиеновые звенья различной длины.

1. Introduction

Low-density polyethylene (LDPE) belongs to the linear carbon chain molecules and is characterized by low mechanical, optical, and electrically conductive properties. Modifications of this polymer and improvement of these properties can be achieved by doping the matrix with various fillers [1–7]. Of particular interest are carbon systems, such as carbon nanotubes (CNTs) [2]. At the same time, in nanocomposites including CNTs, the formation of a conductive cluster can be inhibited due to the absence of ohmic contact in the case of coating the fillers with a polymer matrix. Therefore, there is a necessity to modify the polymer matrix of the composite with an additive that would reduce the contact resistance by increasing the tunneling of the charge carriers.

Such additives can be a variety of dyes, including methylene blue (MB) with a developed π-conjugate system [8–9]. The introduction of various dopants can significantly affect the mechanical properties; therefore, it is important to choose such conditions for the formation of composites, which would improve their mechanical properties [4, 10–13]. It is important to determine the mechanisms of this improvement, using a comparison of mechanical properties with increasing dye content and using optical methods such as Raman scattering and photoluminescence (PL).

The purpose of this work is to study the dependence of the structure and mechanical properties using the Raman and PL spectra in LDPE-MB composites with changing the dye concentration and to establish mechanisms of improving the mechanical properties of these systems.

2. Experimental

Low density polyethylene composites with methylene blue (MB) dye ($C_{16}H_{18}ClN_3S$) were obtained by hot pressing. To obtain nanocomposites (LDPE-MB), high-pressure (low-density) polyethylene powder was mixed thoroughly with the appropriate amount of dye. The temperature was 125–130°C. The obtained LDPE-MB composites had the appearance of discs with a diameter of 30 mm. The concentration of nanotubes in the polymer matrix was from 0 to 0.070 vol. fract.

For the investigation of mechanical properties of nanocomposites LDPE-MB, an ultrasonic KERN-4 computerized velocity meter was used.

The dynamic elastic Young's modulus was determined by the formula:

$$E = \rho V_l^2, \qquad (1)$$

where ρ is the sample density, V_l is the velocity of quasi-longitudinal ultrasonic elastic waves.

The dynamic shear modulus was obtained by the formula:

$$G' = \rho V_{tr}^2, \qquad (2)$$

where V_{tr} is the velocity of quasi-transverse ultrasonic elastic waves.

The Poisson's coefficient was calculated from the equation:

$$V' = \frac{\frac{1}{2} V_l^2}{V_{tr}^2}. \qquad (3)$$

Raman spectra were measured at room temperature in the reflection geometry using a Horiba Jobin Yvon T64000 triple spectrometer equipped with a cooled CCD detector. The spectra were excited by an Ar–Kr ion laser with a wavelength $\lambda_L = 488$ nm. Continuous He–Cd laser lines with wavelength $\lambda_L = 325$ nm were used to excite photoluminescence spectra.

3. Results and discussion

In the solid state, the methylene blue dye (MB) is a crystalline phase that described by the monoclinic structure. In the low-density polyethylene (LDPE) with dye, the crystalline structure remains unchanged. There is only a slight restructuring of the crystallinity, which increases with a low MB content and decreases with increasing dye concentration (Fig. 1).

This dependence is due to the fact that at lower concentrations, the dye acts as the
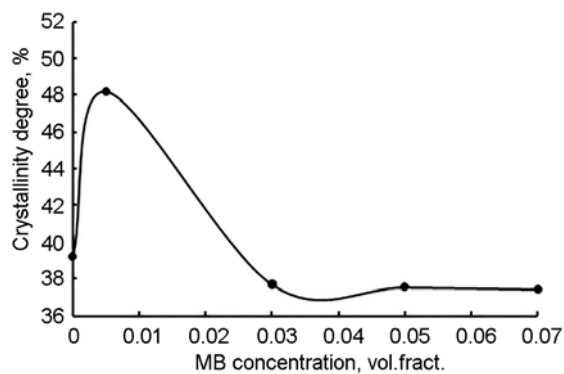
Fig. 1. Dependence of crystallinity degree versus MB concentration in LDPE.

center of crystallization in the polymer matrix. With increasing concentration of the dye, its aggregation is observed.

It should be noted that the concentration dependence of the elastic modulus, shear modulus, Poisson's coefficient in the presence of MB differs from the behavior of these parameters in the LDPE-carbon nanotube composites [11–13]. If in nanocomposites with a lower concentration of nanotubes, the moduli correlate with a change in the degree of crystallinity; then in nanocomposites with MB, the elastic modulus, shear modulus, and Poisson's ratio decrease, and with an increase in the MB content, a maximum of these values appears (Fig. 2).

It is evident that the presence of three regions of change in the elasticity and shear moduli, in which their fall and rise are observed, has little to do with changes in the degree of crystallinity and is due to structural, and possibly conformational and defective transformations in the amorphous polymer phase. In the interval of lower MB concentrations, the doping of additives with smaller physical and mechanical characteristics leads to a decrease in the values of
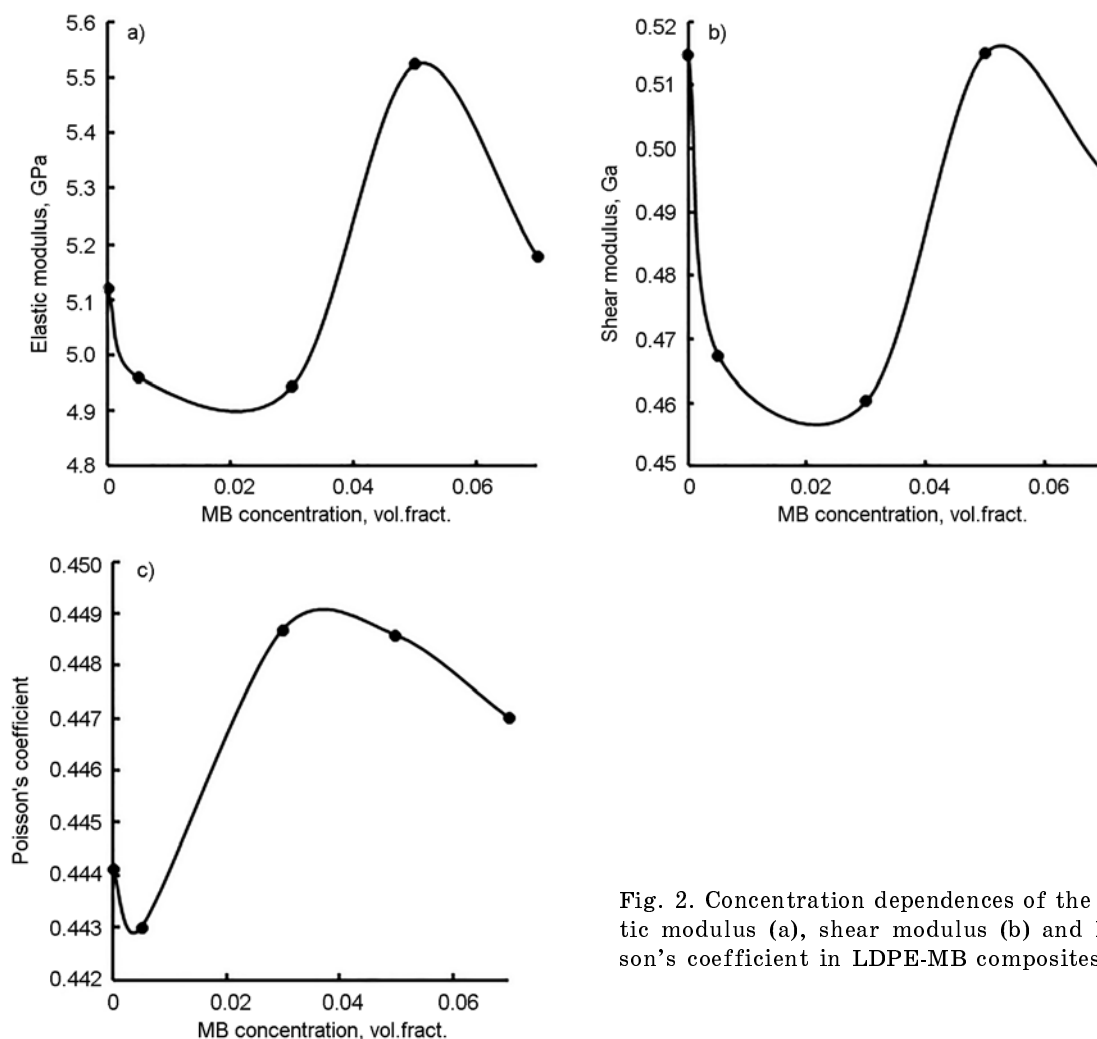

Fig. 2. Concentration dependences of the elastic modulus (a), shear modulus (b) and Poisson's coefficient in LDPE-MB composites.
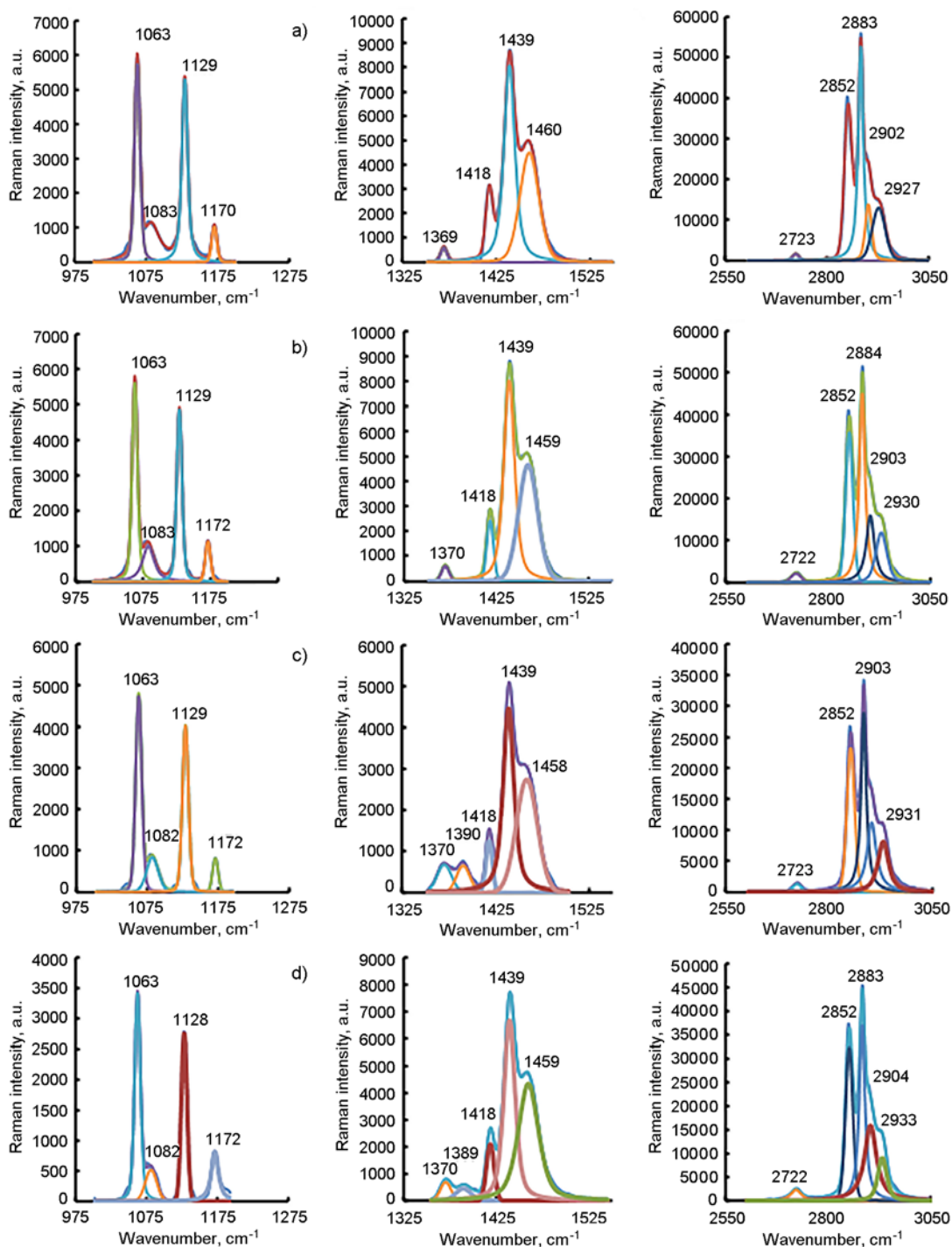
Fig. 3. Raman spectra in different regions of wavenumbers for LDPE-MB composites with 0 (a), 0.005 (b), 0.03 (c), 0.07 (d) vol. fract. of MB content.

these moduli. In the second stage, immobilized polymer layers are formed on the additives. The interaction of polymer chains with the surface of the dye particles includes their partial orientation and leads to an increase in both moduli. With the further increase of the additive content, their aggregation takes place, which is accompanied by a decrease in the volume of the structured layers; as a result, the mechanical characteristics of the modified polymer matrix are reduced.

Besides, one of the important reasons for the decreasing and rising of mechanical

moduli could be a change in the formation of a segregated structure [14, 15]. In this case, a change in the local concentration of the additive in the interblock space of the polymer matrix can occur. This change in concentration can affect the interaction of the ultrasonic wave with the segregated structure of the composite and the speed of its passage.

Such a rearrangement of the polymer structure occurs as a result of interaction with the surface of the dye particles and should be accompanied by a change in the vibrational Raman spectrum with an increase in the MB content.

Fig. 3 shows different regions of the wavenumber of Raman spectra for LDPE-MB composites with different dye contents.

The most intensive bands in the Raman spectrum are due to deformation vibrations, oscillations, stretching for the C–C bonds in the skeleton, methylene CH_2 — and methyl CH_3 — groups in different amorphous and crystalline phases, trans-conformations of the chain and its orientation [16–22].

Regardless of the dye concentration, the Raman spectra change little in contrast to similar spectra of LDPE filled with carbon nanotubes. At the same time, for the composite with 0.03 vol. fract. of MB, there is an additional band about 1390 cm^{-1}, the peak intensity of 1418 cm^{-1} decreases relative to the band intensity of about 1439 cm^{-1}, and the intensity ratio I_{1418}/I_{1296} decreases. These changes, on the one hand, indicate a decrease in the degree of crystallinity in polyethylene, and on the other hand, the rearrangement of its structure.

For composites with 0.05 and 0.07 vol. fract., the transformation of the vibrational modes of stretching of the CH_2 groups, about 2851 cm^{-1} and 2884 cm^{-1}, begins. It is seen that the intensity of the band 2851 cm^{-1} increases, which indicates the formation of linear chains with trans-conformation. A band of about 1389 cm^{-1} remains, the intensity of the band 1418 cm^{-1} increases. Thus, an intermediate phase with oriented polymer chains is formed in the composite. It can be assumed that such a phase appears in the immobilized layer on the surface of the dye particles. Its formation contributes to the growth of shear and elastic moduli in the composite with 0.05 vol. fract. MB. For the composite with 0.07 vol. fract. MB, intense bands at 1129 cm^{-1} and 2852 cm^{-1} decrease, which indicates a decrease in the volume of the intermediate phase and, as a consequence,
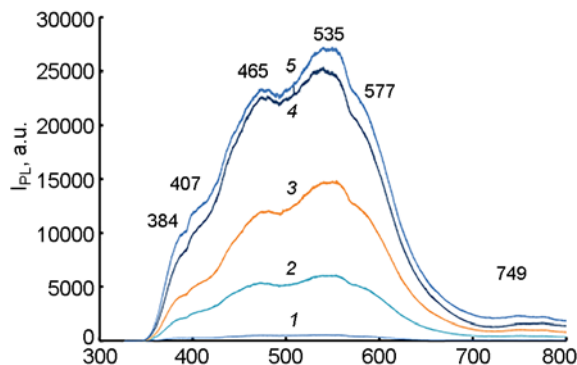

Fig. 4. Photoluminescence spectra of LDPE (*1*) and LDPE-MB composites with 0.005 (*2*), 0.03 (*3*), 0.05(*4*), 0.07 (*5*) vol. fract. of MB content.

the moduli of composites with a high dye content also begin to decrease. Confirmation of the formation of an intermediate phase on the surface of the dye particles, i.e. an amorphous phase with oriented chains, which has little effect on the change in the degree of orthorhombic crystalline phase of polyethylene, can be a significant increase in photoluminescence (PL) in the area associated with the presence of photo-oxide defects, carbonyl groups $C = O$ and polyene structures [35].

Fig. 4 shows PL spectra for pure LDPE and its composites with different content of MB dye.

It is seen that as the dye concentration increases, the PL intensity increases. In general, the PL spectrum for all composites is similar to the PL spectrum of pure LDPE and is a consequence of an increase in the concentration of photo-oxide and polyene defects. Since such defects are characterized by the presence of conjugated bonds in the skeleton of the chain, their appearance also stimulates an increase in the values of the composite moduli.

4. Conclusions

The filling of LDPE with methylene blue dye does not change the crystalline orthorhombic structure of the polymer and leads to a slight change in a degree of crystallinity with increasing concentration of the additive. However, an increase in the dye content is accompanied by a non-monotonic change in the dynamic elastic modulus shear modulus and Poisson's coefficient.

As the content of the dye increases, the intermediate phase with the oriented polymer chains is formed as a result of the interaction between polymer and the dye

surface. This phase is enriched with photo-oxidative and polyene defects in the structure of polyethylene. The formation of this layer with the intermediate phase leads to an increase in the dynamic moduli in the limited concentration range.

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