<u>Regular Article</u>



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# Mechano-Optical Study of the Deformation of Polymer Films

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This work examines the optical properties and surface morphologies of polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) films using infrared (IR) spectroscopy. IR spectroscopy could identify absorption lines attributed to various functional groups and those associated with lower-density linear polyethylene. The specific characteristics of IR spectra for linear low-density polyethylene were influenced by polymer processing conditions, branching, and monomer content. Moreover, the IR spectrum of PVC showed valuable information about its molecular structure and composition. Comparatively, polypropylene (PP) films exhibited higher absolute light transmission in the ultraviolet and visible spectrum when contrasted with films based on PE and PVC. The results of atomic force microscopy (AFM) and IR spectroscopy revealed that heat-induced decomposition and subsequent cooling did not impact the surface roughness or thickness of the films, confirming the retention of structural and electrophysical properties.

Keywords: Polymer, Polyethylene, Polypropylene, Polyvinylchloride, Film, Properties, Deformation, Optical, Birefringence, Microscopy, Infrared, Spectroscopy, Polarization

## INTRODUCTION

Due to the wide use of polymer films in various industries, their production volumes are increasing every year. The main requirements for polymer films during production are physical properties (especially strain strength), light resistance (optical properties), heat resistance (thermal properties), high stability, and environmental safety [1]. These properties of polymeric materials depend not only on the technological processes of their production, but also on the molecular structure and low molecular weight structure of polymeric materials, electrical and physical processes, their service life, and their physicochemical composition, which is determined under the influence of the atmosphere [2]. Therefore, the study of the properties that determine the optimal order of operation of polymer films, the period that guarantees the suitability of polymer materials for practical use to select the types of their modification, is an important subject [3].

The novelty of this work is due to several key aspects: First, we determined the operational longevity of domestic plastic films, encompassing polyethylene, polypropylene, and polyvinyl chloride, while considering their distinctive properties. In addition, by subjecting these films to stretching, we unveiled their enhanced flexibility due to structural alterations, where the extent of stretching and breaking correlates with their light-modifying effects. Specifically, our study showed that polypropylene (PP) films allow greater sunlight transmission compared to the counterparts made of polyethylene (PE) or polyvinyl chloride (PVC). Employing a specialized method, we investigated film structure and discerned that heating and subsequent

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cooling have negligible impact on thickness and surface characteristics, reaffirming their robustness. Due to the strength of the chemical structure of polymer films and the fact that they are destroyed very slowly in natural conditions over several decades, its disposal after a period of use is very important. In this case, it is necessary to study the strength, optical, thermal, and special properties of polymer films for modified polymer composites, which are actively used in practice.

# THE LEVEL OF KNOWLEDGE OF THE PROBLEM

In many countries of the world, scientific research works are carried out at an accelerated pace to obtain flat thin-film polymeric materials with different surface structures to study their physicochemical properties and their practical use.

In many of the published articles, the mechanical strength of mainly thin-layer materials is devoted to determining their physical properties through research using a disconnecting machine. For the development of radiostructural analysis of decay and orientational crystallization in the deformation stretching of lamellar layers of polyethylene film, A. Keller, S.Ya. Frenkel, Y. Podvigalkin, A.A. Tager, I.I. Perepechko and a number of scientific schools have made significant contributions [4-5].

In the development of this direction in Uzbekistan, S.Sh. Rashidova, S.S. Negmatov, N.R. Ashurov, A.A. Kholmuminov and other experienced scientists made a great contribution with their research [6-7]. They studied the physical and mechanical properties, heat and fire resistance, and other properties of polymer films with special physical and chemical properties. Prior to these studies, there were scientific research works in the literature related to the development of technical conditions for the control of reversible and irreversible deformation changes in thin-layer polymeric materials, control of deformation changes in polymer films by the polarization-optical method, practical use of films and determining their resistance to external mechanical influences [8]. Currently, polymer films are used in agriculture, food, industrial technology, medicine, pharmaceuticals, plastic packaging systems, construction, household, and as components of various products such as furniture or electronics, lamination of cardboard and other materials, composites and many other areas. Hence, the study of their physical and operational properties and the search for optimal solutions is one of the most important and urgent tasks [9].

## **OBJECTS AND METHODS OF RESEARCH**

#### **Polyethylene Film (PE)**

A thin transparent film was chosen based on polyethylene produced by the Shurtan Gas Chemical Combine grade F-Y 240. It is known that polyethylene is a relatively simple highmolecular compound with a monomer link:

$$[-CH_2 - CH_2]_n$$

The mass of the monomer link is  $M_0 = 28$ , which is much less than that of other polymers. The molecular chain of polyethylene defines its resistant to chemical and environmental influences, for example, it does not melt at temperatures below 80 °C. But under external physical influences, it is very plastic, easily subjected to structural changes. It exists in highly crystalline and amorphous states. Lamells, fibrils, folded and straightened chains can form crystalline structures.

Depending on the brand of polyethylene, it can vitrify at a temperature of about 70 °C, and convert to a liquid state in the range of 105-150 °C. Its density is  $\rho = 0.90-0.96$  g cm<sup>-3</sup>, and the degree of crystallization is in the range C<sub>cr</sub> = 10-70%, A film with C<sub>cr</sub> < 15% can be considered amorphous.

The film obtained on the basis of this polyethylene was thin and transparent, its density was  $\rho = 0.92$  g cm<sup>-3</sup> and refractive index was n = 1,34. Plenkaning kalinliga was d = 25-30 microns atrophida. It could exhibit mechanical and optical anisotropy when stretched in length and width. Such an anisotropic effect is of a complex nature and can be detected and controlled during research using special mechano-optical methods.

**Polypropylene film (PP).** Depending on the grade of polypropylene, a thin transparent film based on polypropylene produced by Uz-Kor Gas Chemical with a density of  $\rho = 0.9$ -0.91 g cm<sup>-3</sup> and grade FC-150B was chosen. It is known that the chemical formula of polypropylene indicate on a high molecular weight compound with a monomer unit shown below:

$$[-C_3H_6 - C_3H_6 -]_n$$

Polypropylene film is one of the modern packaging materials that makes it possible to achieve water resistance and safety of other materials. This material is used in the food industry for the production of various packaging products [10].

Polypropylene film is chemically resistant to high and low temperatures from -80  $^{\circ}$ C to +170  $^{\circ}$ C.

**Polyvinylchloride film (PVC).** A thin transparent film produced by Navoiazot based on PVC-S-6346-M polyvinylchloride, 50-250 microns thick and 125-150 g cm<sup>-3</sup> density was chosen. Chemical formula of polyvinyl chloride:

 $[-CH_2 - CHCl -]_n$ 

Polyvinyl chloride film is elastic, highly translucent, usable in humid conditions, resistant to mechanical stress, stable under temperature changes, and it withstands temperatures down to -15 °C. The addition of plasticizers increases the frost resistance of PVC fil. It is reliable in contact with chemicals such as non-aggressive acids, oils, hydroxides, and minerals, cutting, forming, gluing, welding, and it is fire-resistant (PVC film does not burn at sufficiently high temperatures, but simply melts).

**Polarization-optical method.** In the manufacturring process of polymer film samples, based on the possibilities of polarization-optical control of deformation changes under thermomechanical action, it was taken into account that the film width should be practically equal to the diameter of the microscope objective (0,5 cm). In accordance with this, the samples for research were prepared by cutting along the width, height and diagonal of the film, in the form of films with a width x = 0.5 cm, as shown in Fig. 1.

The section is drawn along the dotted line. In this case, the A4 film was first cut into 4 equal quadrilaterals (stage 1). Then each was cut in different directions (stage 2). A cut in such directions makes it possible to determine the variation of resistance to mechanical deformation by stretching along the length and width of the film, as well as its diagonals.

When cutting such samples, the film should not be subjected to serious deformation changes. Even a slight deformation can cause the appearance of polarization-optical effects in the film. Polymer films are heat-sensitive materials.



Fig. 1. Polymer film cutting drawing and sample preparation.

Usually, at temperatures above 70 °C, it passes into a glassy state, and from 110 °C, the crystalline structure is destroyed and begins to melt. It is very important to consider the impact on the environment, because under normal air conditions, i.e. in an oxygen environment, along with thermochemical destruction, polyethylene melts. Heated oxygen causes chemical changes and decomposition of the film.

Therefore, it is necessary to carry out an experiment in an oxygen-free environment in order to realize the process of manifestation of only thermal changes in the film. To do this, heat treatment was carried out by a special method that almost completely excludes the presence of oxygen. This was done by tightly wrapping the cut samples in aluminum foil.

The samples were kept at 20 °C, 35 °C, 50 °C, 65 °C, and 80 °C for 30 min. Then, they cooled at room temperature for 60 min. After that, the foils were opened and the samples

were gradually removed without damage.

The implementation of mechanical deformation due to external physical forces requires the use of direct dynamometric methods. In this paper, we first considered the deformation changes in the objects of study, analyzing the general scheme of the dynamometric method (Fig. 2).

The physical changes due to mechanical deformation and stretching of the film (3), which depend on the speed of rotation of the matovilon of the drum (4), were measured depending on time (t) on a scale of 5.

This measures how much the film is stretched. However, the force (F) used to implement such a change is determined by the stretching of the sample in time due to stress  $\sigma = F / S$ , which is the change in deformation  $\Delta l = l_i - l_o$ . The change in deformation is measured by the width  $(\Delta l_w)$  and length  $(\Delta l_l)$ of the film, and the mechanical anisotropy  $A_m = A_m = \Delta l_l / \Delta l_w$ is determined from their ratio. anisotropy. This anisotropy largely depends on the conformational state of the molecular chain, and its maximum value is observed when the chain is straightened. Such an observation can be made directly on polymer films by the birefringence method. It is necessary to take into account temperature and external mechanical action, since molecular chains are easily deformed under such external influences; the optical anisotropy is changed as a result of conformational changes [11].

A specially assembled polarization-optical device for carrying out such studies to obtain the changes in optical anisotropies is shown in Fig. 3. In this case, a film of thickness (d) is placed vertically on a liquid-glass thermostat (T), the temperature of which is controlled by a thermometer (T), and polarized light with a wavelength  $\lambda \approx 0.56$  nm and a direction angle  $\varphi_1 \approx 45^\circ$  is directed perpendicular to it.

This beam is formed using a light source (L), a condenser (K) and a polarizer (R). For example, light passing through a fiber is deflected by an angle  $\varphi_2$  depending on the degree of orientational ordering of molecular chains and is measured by the analyzer limb (A) of a polarizing microscope (PM).



**Fig. 2.** General scheme of the dynamometric method for studying the mechanical deformation of a polymer film.

The fact that the elementary unit, segment, and molecular chain of a polymer have specific optical anisotropy means that the materials based on this polymer show optical



Fig. 3. Drawing of a special polarizing optical device.

Here  $(\varphi_l - \varphi_2)$  is the difference between the polarization angles of ordinary and extraordinary rays. Based on this, the refractive index of the double beam  $(d_n)$  is calculated as follows:  $\Delta n \approx \lambda (\varphi_1 - \varphi_2)/180 d$ 

The orientation factor  $(\beta)$  of polymer molecules is determined by the following relation

$$\beta \approx (\Delta n / \Delta n_o)^{1/2}$$

In above formula,  $\Delta n_o$  is the initial birefringence of the polymer molecules in a solvent-free medium. It is also possible to record an anisotropic image of the material using a digital camera (F).

The polarization optical system of this instrument allows one to carry out studies by directly measuring the magnitude of birefringence in a medium without a solvent or with a solvent at various temperatures. Anisotropic effects are observed using a polarizing microscope [12].

Its value is defined as the effect of birefringence ( $\Delta n$ ). In this case, when a monochromatic beam with a certain wavelength ( $\lambda$ ) is transmitted through a material with a small thickness (d), in the range of micro and less, ordinary ( $\varphi_o$ ) and extraordinary ( $\varphi_l$ ) beams are observed with a difference  $\Delta \varphi = \varphi_o - \varphi_l$ , and they are measured with a special limb instrument and calculated using the following formula:

$$\Delta n = \lambda \Delta \varphi / 180 d$$

The ratio of the value of this parameter obtained from measurements ( $\Delta n$ ) to the maximum value of birefringence calculated semiempirically ( $\Delta n_{\infty}$ ) gives the orientation coefficient of macromolecules ( $\beta$ ):

$$\beta \approx (\Delta n / \Delta n_{\infty})^{0.5}$$

The value of  $\Delta n_{\infty}$  for a number of polymer solutions was determined by the Peterlin formula.

$$\Delta n_{\infty} \approx 2\pi (n^2 + 2)^2 (9n)^{-1} (a_1 - a_2)N'$$

where *n* is the refractive index of the solution;  $N' = {N_A C}/{M_0}$ and C is concentration. In the solid phase, density ( $\rho$ ) is used instead of C.

In the general case,  $\Delta n / \Delta n_{\infty}$ , that is the orientation factor  $\beta = \left[\frac{\Delta n}{\Delta n_{\infty}}\right]^{0.5}$ , allows us to analyze the morphological

description of the supramolecular structure of polymers based on the control of changes in their optical anisotropy using the birefringence method [13].

Single-layer polyethylene (PE), polyvinyl chloride (PVC) and polypropylene (PP) films with different in-plane thicknesses were selected for this research. The samples had a length of 5 cm, a width of 1 cm and a thickness of  $(10-400) \mu m$ , and their structural appearance was first studied using a polarizing optical microscope (POM).

The polymer films were transparent. The measurements showed that the thickness was 50 µm (measurement error  $\pm 2 \mu$ m) and the difference between polarized optical beams, which were normal ( $\varphi_0$ ) and abnormal ( $\varphi_l$ ) rays, was  $\Delta \varphi = \varphi_0 - \varphi_l = 2^\circ$  (measurement error  $\pm 0,01^\circ$ ).

The device consisted of mechanical and optical parts, and in the mechanical part, the sample wasis uniformly pulled from the end of the film in the vertical direction and deformed to break. In the optical section, polarization-polarized light crossed the sample film in a perpendicular direction, that was in the horizontal direction. Using a polarizing microscope, optical anisotropic effects in the film and the birefringence index were measured (Fig. 4). One end of the sample - thin

<ol> <li>1- Thin sample of material;</li> <li>2- Polarizer;</li> </ol>
<ul> <li>3- Analyzer;</li> <li>4- Eyepiece;</li> <li>5- Adjustment knob;</li> <li>6- D (electronic scale);</li> <li>7- Reel drum;</li> <li>8- Electric motor;</li> <li>9- Scale (micromillimeter);</li> <li>10,11- Cable (with clamp)</li> </ul>

**Fig. 4.** Specially assembled "mechano-optical" device (a) and a schematic drawing of deformation changes in it (b).

film material (1) was clamped on the rope (10) of electronic scales (6) used as a dynamometer in the mechanical part, and a thin rope (11), which is tensioned due to the rotation of the balance. drum-reel (7) was pressed to the other end.

Initially in state A, there was no mechanical stress at the ends of the film ( $\sigma_1 = \sigma_2 = 0$ ), and its length ( $l_1$ ), width ( $l_2$ ) and thickness (d), total characteristic surface  $S_t = l_2 \cdot d$ , volume  $V_t$  and mass  $m_t$  did not change.

Then, in case B, the drum-reel rotated with the same frequency ( $V_a$ ) and the condition  $\sigma_1 < \sigma_2 \neq 0$  was satisfied, the film began to stretch along the length of the dynamometer towards the drum-reel, and the parallelepiped-shaped (A) shape turned into a conical (B) shape and became thinner as it was continuously stretched. When the length of the conical film ( $l_1$ ) reached the critical value  $l_1 = l_{cr}$ , the conditions  $l_2 \rightarrow 0 \ \text{m} \ d \rightarrow 0$  were met and the film broke. The characteristic  $S_t$  rectangular surface, due to the change in deformation, turned into a round surface  $S_a = \pi \left(\frac{d}{2}\right)^2$ ,

During deformation stretching, the mass  $m_t$  of the film did not change, but the sample size ( $V_t$ ) decreased due to the deformation-orientational ordering and densification of structural elements.

In the optical part, the film sample (1) was placed perpendicular to the polarized monochromatic light between the polarizer (2) and the analyzer (3). The wavelength of light was l = 560 nm; it was separated by a ZhZ-6 filter and passed through a polaroid, a sample, a lens, an analyzer and an eyepiece (4) into one line, transforming into a parallel lens beam. Light was polarized in a polaroid, which was divided into ordinary and extraordinary rays.

A normal beam was bent through a certain angle  $\varphi_l$  due to deformational stretching of the sample (a change in the shape and arrangement of its constituent elements), which was visually observed through the eyepiece as an optical anisotropic effect [14]. The analyzer was equipped with a special conical dial to measure the differences between ordinary and unusual rays, that was between the optical "black" background ( $\varphi_o$ ) and the "bright" area ( $\varphi_l$ ) in the center, the optical anisotropy ( $\Delta \varphi$ ), as well as the film thickness (*d*) using a microscale in the eyepiece.

According to the formula for determining the birefringence index  $\Delta n_m = \lambda \Delta \varphi / 180^{\circ} d$ ) used above, the birefringence index of the sample film in the initial state was

 $\Delta n_0 = \lambda \Delta \varphi_0 / 180^{\circ} d_0$ , and its amount with a change in deformation was taken as  $\Delta n_i = \lambda \Delta \varphi_i / 180^{\circ} d_i$  and the orientation coefficient ( $\beta$ ), anisotropic characteristics, was determined by their ratio:

$$\beta = \left[\frac{\Delta n_i - \Delta n_0}{\Delta n_i}\right]^{0.5}$$

In this sense, this "mechano-optical" device was assembled on the basis of standard "cutting machines" and their general principle of operation. Therefore, the measurement values of the "mechano-optical" device were calibrated according to the results obtained on standard cutting machines. During deformation stretching of the samples along the "length" and "width", the values of "tensile strength" ( $\sigma_l$ , MPa and  $\sigma_w$ , MPa) and relative elongation indices ( $\varepsilon_l$ , % and  $\varepsilon_w$ , %) were determined.

$$\sigma_r = F_r / A_0$$
$$\varepsilon_r = \frac{\Delta l_{or}}{l_0} \cdot 100\%$$

In above formulations,  $F_r$  – is the tensile stress at break, N;  $A_0$  – is the initial cross section of the sample, mm<sup>2</sup>;  $\Delta l_{or}$  is sample length change at break, mm;  $l_0$  is the initial length of the sample, mm. The unit of strength is N/mm<sup>2</sup>, taken as MPa for the SI system. The experiments were carried out on thin polymer films of three different ( $\omega$ ) modes and different thicknesses (d), in the longitudinal and transverse directions, at a rotational speed of the drum-motor of the mechanooptical device  $\omega = 1 \text{ cm/s}$ . [15].

Method of atomic force microscopy (AFM). Atomic force microscopy (AFM) is one of the analytical methods used to measure differences in the height and width of materials in the nanoscale range. Atomic force microscopy is an amazing method that allows us to see and measure the surface structure of a sample with high resolution and accuracy. It is also an excellent tool for analyzing the phase morphology of microphase-separated block copolymer systems or other nanoscale products. Many examples require an individual approach to apply the ACM method. The sample must be immobilized on a flat substrate. Since the maximum scanning height is approximately 10  $\mu$ m, it is necessary that the sample be flat within the scanned area [16]. Using AFM, one can study the surface (morphological) properties of micro- and nanostructured materials with a size of almost 1A (angestrom) and make their adequate assessment.

Van der Waals interactions or electrostatic attraction (repulsion) are measured in AFM, where a probe called a cantilever is a thin needle fixed vertically to a thin elastic light.

Simply put, the method is based on registration of the attraction or repulsion of sample and probe atoms. The laser beam is directed to the end of the beam carrying the console, is reflected from the surface and enters the center of the recording device, divided into four sectors. Depending on the change in the force of interaction between the console and the surface, the beam carrying the probe bends, the laser beam deviates from the central position and becomes one of the sectors of the detector. The feedback system changes the position of the console, returning it (and the laser) to the "zero" center position [17].

Thus, by registering the offset of the cantilever required to return the laser to the "zero" point, the topology of the system surface is measured.

To determine the morphological characteristics of polymer films, studies were carried out using Agilent 5500 atomic force microscopy [18].

Infrared (IR)-spectroscopic method of analysis. Infrared spectroscopy (IR spectroscopy), along with combined scattering spectroscopy (CSR), makes it possible to determine the chemical composition of objects. The penetration depth depends on the absorption coefficient of the material under study and is about 1  $\mu$ m for high molecular weight solids. It allows one to determine the optical characteristics, thickness, and surface morphology of thin films.

By comparing the IR spectrum of an unknown substance with the spectrum of a known substance in the obtained IR spectrum images, one can prove their similarity. If the spectra do not match, but many of the properties of both substances are close to each other, then it is clear that this new substance is not sufficiently purified [19].

Thus, IR spectroscopy also makes it possible to determine the degree of purity of substances. Which groups are present in the molecule of an unknown substance, or which bonds are formed (or lost) in the molecule as a result of the reaction, is determined by observing the absorption maximum of these bonds in the IR spectrum. In addition, using IR spectra, one can obtain information not only about a particular group, but also about its side groups. The maximum of a given group varies slightly depending on which atoms and groups surround it [20].

IR spectroscopy is used for the qualitative and quantitative study of reversible organic reactions. To do this, the absorption intensity in the spectrum is compared with the absorption intensity of the individual components. Using IR spectroscopy, one can draw a conclusion about the configuration and conformation of the molecule.

## **RESULTS AND DISCUSSION**

Films based on polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) prepared at a temperature of  $(180 \pm 10)$  °C and a pressure of (1-2) 10<sup>5</sup> Pa. Physical and mechanical properties of these polymer films are presented in Table 1.

The dependence of mechanical and optical properties upon deformation of polymer films largely depends on the conformational and configurational state of the molecular chain of the polymer, and its maximum value is observed when the chain is straightened. Such an observation can be made directly on polymer films by the birefringence method. It is necessary to take into account temperature and external mechanical action, since molecular chains are easily deformed under such external influences; they change their optical properties-optical anisotropy as a result of conformational changes [21]. For experimental studies, film samples were cut out with a width  $l_2 = 1$  cm and a length of 7 cm.

These samples were attached to the grips of the mechanooptical device at a distance of 1 cm from the ends, while making sure that the deformation-tensile working part of the sample film was  $l_1 = 5$  cm.

The values of tensile strength ( $\sigma_l$ , MPa and  $\sigma_w$ , MPa) and relative elongation indices ( $\varepsilon_l$ , % and  $\varepsilon_w$ , %) were determined under strain of samples along the length and width. For this, the following formulas were used:

$$\sigma_r = F_r / A_0$$

N⁰	Samula dasiawatiaw	Breaking stress	Elongation at break	Elastic modulus	
	Sample designation	$\sigma$ (MPa)	e (%)	E (MPa)	
1	PE (Shurtan GCC)	$14.1 \pm 2.5$	$743\pm73$	$95 \pm 11$	
2	PP (Uz-Kor Gas Chemical)	$35.17\pm0.25$	$870.55 \pm 40.25$	$943.00\pm33.16$	
3	PVC (Navoiazot)	$32.79 \pm 1.78$	$183.47 \pm 24.36$	$253.04\pm36.27$	

Table 1. Physical and Mechanical Properties of the Polymer Films

Table 2. Tensile Strain Indices for Polymer Films

		Film tear rates					_		
C1-	d	With longitudinal stretch			With transverse stretch			_	
Sample	(µm)	$\sigma_l$ (Mpa)	$\mathcal{E}_{\scriptscriptstyle W}\left(\% ight)$	$\beta_l$	k (MPa)	$\mathcal{E}_{\scriptscriptstyle W}\left( ^{0\!$	$\beta_w$	A <sub>m</sub>	A <sub>o</sub>
PE (Shurtan GCC)	200	14	552	0.74	11	557	0.65	1.27	1.14
PE (Uz-Kor Gas	100	32	401	0.81	23	308	0.61	1.39	1.33
PVC (Navoiazot)	50	34	302	0.91	25	221	0.49	1.36	1.86

$$\varepsilon_r = \frac{\Delta l_{or}}{l_0} \cdot 100\%$$

where  $F_r$  is the tensile stress at break, N;  $A_0$  is the initial cross section of the sample, mm<sup>2</sup>;  $\Delta l_{or}$  is the sample length change at the moment of fracture, mm;  $l_0$  is the initial length of the sample, mm.

The mechanical anisotropy  $A_m = \frac{\sigma_l}{\sigma_w}$  and the optical anisotropy  $A_o = \frac{\beta_l}{\beta_w}$  of the samples were also determined. The results are presented in Table 2.

A comparative analysis of the results showed that the values of the ultimate strength and the relative elongation in tension of the film samples along the length and width were close to each other, and the mechanical and optical anisotropies were in the range of 1.27-1.86. It was observed that when the samples were deformed, they changed from a parallelepiped to a conical (prism) shape, exhibiting anisotropic effects due to the deformation-orientational ordering of the macromolecules.

In films, the orientation factor ( $\beta$ ) is proportional to the relative strain elongation ( $\epsilon$ ); the optical anisotropy is expressed by the linear dependence  $\beta = k\epsilon$ . Because of the film deformation, the lamellar

supramolecular structure is deformed and passes into a highly elastic state, and it has been found that the critical parameters of rupture and relative elongation depend proportionally on optical anisotropic effects. Thus, it has been established that under symmetrical stretching of a thin-film tape, depending on the stretching stress, the elements of the tape structure undergo a strong deformation change, delamination, and destruction, and these processes proceed synchronously depending on the optical anisotropy. The relation function of the orientation factor ( $\beta$ ) with relative strain ( $\varepsilon$ ) by optical anisotropy is plotted as  $\beta = k_1 \varepsilon = 0.001 \varepsilon$  for segmental changes and  $\beta = k_2 \varepsilon = 0.004 \varepsilon$ for molecular displacements. In a large relative elongation field  $\varepsilon > 430$  %, optical anisotropic effects of different colors turn white and break the films.

These anisotropic effects indicate the isotropy of these films, since the indices are almost uniform along the length and width of the sample.

Bending, twisting and stretching of internal bonds in a polymer film molecule mainly consists of three characteristic sections. The I-characteristic region has a linear form and corresponds to Hooke's law, that is, the stress-strain is linearly proportional. In this case, the internal bonds in the polymer molecule are bent, twisted and stretched, but the macromolecules do not move relative to each other. Such changes are fast and reversible processes, and the deformation is elastic. On the whole, it was obtained that in the I-region, Young's modulus of elasticity was approximately equal to  $E \approx 20$  MPa.

In the II-descriptive region, there is a deviation from the linear relationship, and this point is also called the proportional limit. In this part, deformation occurs with spreading and straightening of folded macromolecules. In this case, the macromolecules do not move relative to each other, and the deformation change is reversible and occurs relatively slowly.

Within the III-descriptive area, fluidity occurs, that is, the deformation change is carried out by the layer-by-layer movement of macromolecules relative to each other, the process is irreversible, and the achieved deformation changes are preserved (Fig. 5).

In our next work, the spectral transmission characteristics of polymer films were obtained in the form of a dependence of the transmittance (t) on the wavelength ( $\lambda$ ) after irradiation with a mercury lamp with duration (t) = 5, 10, 15, 25 and 40 h. The values of the transmittance (t) for the polymer films studied by the polarization-optical method were  $\lambda = 350$  and 430 nm (in the ultraviolet and visible regions of the spectrum, respectively) and the magnitude of the absolute change in the transmittance after exposure to radiation (t) = 10 and 40 h was determined (shown in Table 3).

This table shows that the film based on polypropylene (PP) had a higher absolute light transmission compared to films based on polyethylene (PE) and polyvinyl chloride (PVC) in the ultraviolet and visible spectral regions. For all polymer films, after a time (t) = 10 and 40 hours, the transmittance (t) decreased significantly in the ultraviolet region of the spectrum for a film based on polyvinyl chloride (PVC).

The spectral characteristics of light absorption in polymer films (D) were measured as a function of optical density  $\lambda$  (Fig. 6).



**Fig. 5.** Dependences of the orientation factor ( $\beta$ ) on the relative strain ( $\epsilon$ ) for a polyethylene film.



**Fig. 6.** Schematic representation of light transmission through a polymer film sample.

D - 1 £1	τ (%)	$\lambda$ (nm)	τ (%)	t = 10 h	τ (%)	t = 40 h
Polymer films	350	430	350	430	350	430
PE (Shurtan GCC)	62	76	2	0	8	2
PP (Uz-Kor Gas Chemical)	78	84	5	0	-	-
PVC (Navoiazot)	78	80	12	1	22	3

**Table 3.** Values of the Electrical Conductivity of Polymer Films after (t) = 10 and 40 h

They are related to the function  $D = f(\lambda)$ , and we express it in terms of  $D = lg \frac{I}{I_0}$ . Here I<sub>0</sub> and I are the intensity of the light rays incident on the polymer film and passing through it, respectively.

Based on the Bugert-Lambert-Beer law  $I = I_0 e^{-k_\lambda \chi}$ , where the optical density is  $D = k_\lambda \chi$ , we obtained that they were related.

In the ultraviolet and visible regions of the spectrum (Fig. 7), after t = 10 and 40 h, these values were found: for polyethylene  $D_{PE} = 2.8$ , for polypropylene  $D_{PP} = 2.0$ , and for the films based on polyvinyl chloride  $D_{PVX} = 0.96$ .

Thus, we obtained that mechanical deformation changes in thin films based on polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) were dependent internally on the polarization-optical properties of these materials.

Surface Structure and Morphological Characteristics of Polymer Films. The properties of films consisting of polymeric macromolecules of the same chemical structure can vary greatly. This difference in properties is largely due to the arrangement of macromolecules in them. Due to the forces of intermolecular interaction in the processes of film formation, not only individual molecules are located relative to each other, but also various supramolecular structures can arise in the form of aggregates of macromolecules.

The concepts of supramolecular structures are based on the results of studies that make it possible to establish the presence of domains of different levels of order in the bulk of the polymer. In order to reveal the features of the influence of high temperatures on the supramolecular structure, a number of studies were carried out to study the supramolecular structure of submicron films induced by thermal heating at temperatures close to the temperature of polymer decomposition.

A large number of measurements showed that heating film samples in air to a temperature of 350 °C and subsequent cooling did not affect the surface roughness and did not change the thickness of polymer films. The same structure and electrical characteristics were preserved. It was found that the temperature of the beginning of the decomposition of the polyethylene film was 430 °C. Studying the thermal decomposition of the film within 3-5 min showed that the surface morphology of the polymer chains changed



**Fig. 7.** Dependence of optical density on the wavelength of light.

significantly, and this process could be obtained even with the naked eye.

Such changes in the structure of PE, PP, and PVC films upon heating in air indicate the effect of oxygen on the object under study, which is in agreement with the literature data. Figure 8 shows the AFM images of sections of polymer films with traces of the effects of thermal oxidative degradation.

By reducing the scanning area, a clear image of the structure formed on the surface of the film can be obtained. The surface morphology was a granular structure with structural elements 6-15 nm in size. As a control experiment, the polymer film was fired at 500 °C in vacuum to demonstrate the action of active oxygen. In this case, the film thickness was not decreased and no granular structure was observed, as in previous experiments. In this case, small changes in surface roughness occurred and small cracks appeared. This indicated the beginning of melting and graphitization of polymer films.

Analysis of infrared spectra of polymer films. Infrared spectroscopy (IR spectroscopy), along with combined scattering spectroscopy (CSS), makes it possible to determine the chemical composition of objects. The penetration depth depends on the absorption coefficient of the material under study and is about 1  $\mu$ m for high molecular weight solids. It allows one to determine the optical characteristics, thickness, and surface morphology of thin films.

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**Fig. 8.** AFM images of domestic (from left to right) polyethylene, polypropylene and polyvinyl chloride polymer films, respectively.

In this research work, the absorption spectra in both polymers of domestic PE and isotactic PP were studied by IR spectroscopy [22].

IR spectra analyzes were performed for all samples in a wide range of 500-4000 cm<sup>-1</sup>. The structure of the resulting polymer was analyzed by IR spectroscopy.

In infrared spectral images, regardless of the aggregate state of the substance, each line characterizes the intensity of the substance. The IR spectrum is the most convenient modern option for identifying a substance.

It differs in its reliability from simple physical methods such as measuring the melting point, measuring the refractive index, measuring the density, which are used in the identification of a substance. Also, when analyzing the IR spectrum of each substance, it is necessary to take into account which atom or group of atoms they contain and their mutual deformation effect.

In particular, inductive and mesomeric effects affect organic compounds within a molecule. Intermolecular and intramolecular hydrogen bonds cause a shift in the spectral lines of the bonds involved in this bond. Therefore, it is necessary to consider these points in the analysis of the spectra.

The results of the IR spectroscopic study was carried out for PE (Fig. 9), showing absorption bands at 2930 and 2850 cm<sup>-1</sup>, corresponding to the asymmetric and symmetric stretching vibrations of  $CH_2$  groups. It was observed that the deformations of the  $CH_2$  groups at 1465 and 728 cm<sup>-1</sup> corresponded to the oscillations of the pendulum.

The IR spectrum of PVC (Fig. 10) had a vibration

frequency and an absorption line at 2960, 2926 and 2857 cm<sup>-1</sup>, which indicates that the CH<sub>3</sub> molecule corresponds to the stretching vibration of the C–H molecule, and 1429 and 961 cm<sup>-1</sup> correspond to deformations and pendulum vibrations of  $-CH_2$ – groups.

The absorption spectrum at 1118 cm<sup>-1</sup> can be attributed to the stretching vibration of the C-C group. As it is clear from the IR spectra (Figs. 9 and 10), the IR spectra of polyethylene (PE), obtained at the Shurtan Gas chemical complex, and polyvinyl chloride (PVC) obtained at JSC Navoiazot were significantly decreased. After absorption, the intensity of vibrations of C (carbon) decreased in comparison to other bands in the spectrum, which indicates the occurrence of a reverse reaction. A high-intensity peak appeared at about 1500 cm<sup>-1</sup> in polyethylene and 1800 cm<sup>-1</sup> in polyvinyl chloride, which corresponded to the appearance of a new vibration in the C–H bond system in the aromatic nucleus.

As a result of the thermomechanical action, there was a decrease in the water content in the polymer composite sample under consideration, which led to an overall increase in the intensity of the spectrum in the low-frequency region with a change in the peak ratios at 1500 and 1800 cm<sup>-1</sup>, responsible for the valence oscillations of the C-H bond.

IR spectra were obtained from the sample surface at the same point before and after applying mechanical and thermal loads to it. For a more detailed analysis of the presence of conformational rearrangements of PVC, the separation of peaks in the 1500-1800 cm<sup>-1</sup> region was carried out, focusing on the minima of the second derivative, as shown in Fig. 10.

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Fig. 10. IR spectrum of PVC (Navoiazot).

## CONCLUSION

The IR spectroscopy made it possible to draw more detailed conclusion about the optical characteristics and surface morphology of polyethylene (PE) and polyvinyl chloride (PVC) films. In addition to the lower-density linear polyethylene film absorption lines, there may be smaller absorption lines due to other functional groups that may be present as impurities in the polymer. The exact shape and intensity of the IR spectrum of a linear low-density polyethylene film could vary depending on the processing conditions used to obtain the polymer, as well as the degree of branching and monomer content. In general, the IR spectrum of PVC could provide valuable information about its molecular structure and composition. Compared to the films based on polyethylene (PE) and polyvinyl chloride (PVC) in the ultraviolet and visible region of the spectrum, the film based on polypropylene (PP) had a higher absolute light transmission.

The results of studying the supramolecular structure of the films by AFM and IR showed that heating the film samples in air to the decomposition temperature and subsequent cooling did not affect the surface roughness and did not change the film thickness; the same structural and electrophysical characteristics were retained.

## REFERENCES

- Pilgunov, V. N.; Efremova, K. D., The outflow of a viscous fluid through round holes at low Reynolds numbers. *Aer. Sc. J.* 2015, *01*, 31-57. https://doi.org/10.7463/aersp.0115.0775178.
- [2] Davlyud, D. N., et al. Rheological properties and concentration transitions in water-salt solutions of polyacrylamide and anionic (co) polymers of acrylamide. Pro. Nat. Acad. Sc. Belarus Chem. Ser. 2018, 54 (3), 329-337, https://doi.org/10.29235/1561-8331-2018-54-3-329-337.
- [3] Kholmuminov, A. A.; Matyakubov, B. M., Anisotropic properties of nanofiber porous materials of fibroin silk and cotton cellulose. *Mod. Phy. Let. B.* 2021, 35 (16), 2150276. https://doi.org/10.1142/S0217984921502766.
- [4] Frank, F. C.; Keller, A.; Mackley, M. R., Polymer chain

extension produced by impinging jets and its effect on polyethylene solution. *Polymer.* **1971**, *12* (7), 467-473. https://doi.org/10.1016/0032-3861(71)90064-4.

- [5] Hikosaka, M.; Amano, K.; Rastogi, S.; Keller, A., Lamellar thickening growth of an extended chain single crystal of polyethylene (II): ΔT dependence of lamellar thickening growth rate and comparison with lamellar thickening. J. Mat. Sc. 2000, 35, 5157-5168. https://doi.org/10.1023/A:1004804420369.
- [6] Yunusov, K. E.; Sarymsakov, A. A.; Rashidova, S. S., Structure and properties of biodegradable carboxymethyl cellulose films containing silver nanoparticles. *Polym. Sci. Ser. A*, **2014**, *56*, 283-288. https://doi.org/10.1134/S0965545X14030183.
- [7] Abdurazakov, M.; Gomza, Y. P.; Petrenko, S. D.; Ashurov, N. R., *et al.* Physical-mechanical properties and structure of graphite-filled polycaproamide. *Mech. Compos. Mater.* **1988**, *24*, 203-209. https://doi.org/10.1007/BF00608154.
- [8] Kholmuminov, A. A.; Matyakubov, B. M.; Rakhmonov, T. T., Anisotropic, sorption and filtering properties of thin-layer polymer materials. Sc. J., 2021. Chem. Mat. Res. 3 (2).https://doi.org/10.51594/CMSRJ.V3I2.216.
- [9] Umarbek, A.; Vaxitovich, A.; Raximova, Y.; Karabayeva, M.; Saidkulov, D.; Matyakubov, B., An Investigation of the Electrophysical Properties of Composite Ceramic Materials Containing Nickel Nanoparticles. *Phy. Chem. Res.*, **2023**, *11* (2), 231-239. https://doi.org/10.22036/pcr.2022.335151.2063.
- [10] Matyakubov, B. M.; Eslamasov, M., Some characteristics of nanofiber nanoporous materials. *Int. Sci. J. Theor. App. Sci.* **2023**, *10* (114) 301-306. https://dx.doi.org/10.15863/TAS.
- [11] Galay, L.; Cakmak, M., Online Monitoring of Birefringence Developmentin HeatSetting Polymer Films with a Fast Dual-Wavelength Optical Technique.
  I. Uniaxially Oriented Poly(ethylenenaphthalate). J. Poly. Sc: Part B, 2001, 39, 1107-1121. https://dx.doi.org/10.1002/Polb.1087.
- [12] Martins, C. I.; Cakmak, M., Large Deformation Mechano-Optical and Dynamical Phase Behavior in Uniaxially Stretched Poly(ethylene naphthalate). *Macromolecules*. 2005, 38, 4260-4273.

https://doi.org/10.1021/ma047499s.

- [13] Kanuga, K.; Cakmak, M., Nonlinear Mechanooptical Behavior of Poly(ethylenenaphthalate)/Poly(ether imide) Blends. Dynamic Phase Behavior. *Macromolecules*. 2005, 38, 9698-9710. https://doi.org/10.1021/ma0511595.
- [14] Unsal, E.; Cakmak, M., Molecular mechanism of temporal physico/chemical changes that take place during imidization of polyamic acid: Coupled real-time rheo-optical and IR dichroism measurements. *Polymer.* 2014, 55, 6569-6579. https://doi.org/10.1016/j.polymer.2014.09.064.
- [15] Daniels, R.; Morato, E. O.; Yassin, O. A.; Mao, J.; Mutlu, Z.; Jain, M.; Valenti, J.; Cakmak, M.; Nair, L. S., Poly(cannabinoid)s: Hemp-Derived Biocompatible Thermoplastic Polyesters with Inherent Antioxidant Properties. Acs *App. Mat. Int.* **2022**, *14*, 42804-42811. 36112124 https://doi.org/10.1021/acsami.2c05556.
- [16] Cakmak, M., Temporal evolution of structure in uniaxially stretched PET/PEI blends during constrained annealing: A real time birefringence study. *Polymer.* 2016, 97, 569-579. https://doi.org/10.1016/J.Polymer.2016.05.058.
- [17] Chile, L. -E., *et al.* A comparison of the rheological and mechanical properties of isotactic, syndiotactic, and heterotactic poly(lactide). *Macromol.* **2016**, *49* (3), 909-

919. https://doi.org/10.1021/acs.macromol.5b02568.

- [18] Marcott, C.; Lo, M.; Kjoller, K.; Prater, C.; Noda, I., Spatial differentiation of submicrometer domains in a poly(hydroxyalkanoate) copolymer using instrumentation that combines atomic force microscopy (AFM) and infrared (IR) spectroscopy. *Appl. Spectr.* **2011**, *65*, 1145. https://doi.org/10.1366/11-06341.
- [19] Lifeng, C.; Hongbin, L; Xi, Z., Atomic force microscopic (AFM) study on a self-organizing polymer film, *Polymer Bulletin*. **1998**, *41* (6), 695-699 https://doi.org/10.1007/s002890050420.
- [20] Yu, Z.; Liu, X.; Zhao, F.; Liang, X.; Tian, Y., Fabrication of a low-cost nano SiO<sub>2</sub>/PVC composite ultrafiltration membrane and its antifouling performance, *J. Appl. Polym. Sci.* 2015, *132.* https://doi.org/10.1002/app.41267.
- [21] Campanale, C.; Savino, I.; Massarelli, C.; Felice, V., Fourier Transform Infrared Spectroscopy to Assess the Degree of Alteration of Artificially Aged and Environmentally Weathered Microplastics. *Polymers.* 2023, 15 (4), 911. https://doi.org/10.3390/polym15040911.
- [22] Chen, X., et al. Degradation degree analysis of environmental microplastics by micro FT-IR imaging technology. *Chemosphere*. 2021, 274, 129779. https://doi.org/10.1016/j.chemosphere.2021.129779.