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DETERMINING THE INFLUENCE OF SURFACE ENERGY OF POLYMER FILMS ON THE WETTING AND ADHESION OF FLEXOGRAPHIC INKS

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This study investigates the process of wetting and adhesive interaction between flexographic inks and polymer films of different nature and surface structure. An issue related to flexographic printing on polymer films is insufficient surface wettability and low stability of adhesion of the ink layer, which worsens the print quality. This work explores the wetting of the surface of films with liquids of different polarity and with UV flexographic ink.

The equilibrium values of the cosine of the wetting angle for non-polar and polar liquids have been experimentally determined. The $\cos\theta$ values for non-polar liquids are 0.90–0.99, while for polar liquids they decrease to 0.36–0.92 depending on the type of film surface. The thermodynamic characteristics of wetting, in particular the work of adhesion and cohesion, were calculated. It was established that the work of adhesion varies within 45–140 mN/m.

It has been shown that wetting is determined by the ratio of the dispersive and polar components of surface energy. For non-polar liquids, dispersive interactions dominate, while for polar liquids, polar ones. The influence of the structural characteristics of the surface on wetting has been established. The matte polypropylene film is characterized by worse wettability compared to glossy samples.

The components of the surface energy were determined by the Owens-Wendt method, which made it possible to establish their influence on adhesive interaction. The surface energy values of polymer films are 42–53 mN/m, while the proportion of the polar component increases to 0.19 for samples with better wettability. It has been shown that the adhesive behavior of UV flexographic ink is comparable to polar liquids.

The results could be used to predict the wetting of polymer materials and to optimize flexographic printing processes

Keywords: wetting, adhesion, polymer films, polypropylene, polyethylene terephthalate, surface energy, Owens-Wendt-Rabel-Kaelble (OWRK) method

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1. Introduction

Given the current development of printing production and packaging industry, ensuring high quality of printing on polymer materials is of particular relevance. The wide use of polymer films in the production of flexible packaging, label products, and advertising materials is due to their high consumer and operational properties, in particular low weight, mechanical strength, transparency, barrier characteristics, and the possibility of recycling. The most common among such materials are polypropylene, polyethylene, and polyethylene terephthalate films, which are actively used in flexographic printing, in particular with the use of UV inks. At the same time, the specific physicochemical properties of the surface of polymer films significantly complicate the process of forming a high-quality printed impression.

One of the key issues of printing on polymer films is ensuring proper wettability of the surface with ink and the formation of a sufficient level of adhesion between the ink layer and the substrate. Most polymeric materials are characterized by low surface energy, which leads to poor ink spreading, uneven formation of the ink layer, the appearance

of printing defects, and a decrease in the image's resistance to mechanical and operational influences. In this regard, the task of studying the influence of the surface energy of polymer films on the wettability and adhesion of UV flexographic inks is gaining important scientific and practical importance.

In modern research, considerable attention is paid to the physicochemical mechanisms of interaction of inks with polymer surfaces. In particular, the issue of wetting and adhesion on the surface of polymeric materials was considered in papers [1, 2]. Certain aspects of spreading and formation of adhesive contact were studied in [3, 4]. The features of the interaction of flexographic inks with polymer substrates were analyzed in [5, 6]. It was established that the efficiency of ink layer formation is determined by the ratio of the surface energy of the substrate and the surface tension of the ink, as well as the contribution of the polar and dispersion components of the interfacial interaction. To quantify these characteristics, surface energy determination methods are used, in particular the Owens-Wendt-Rabel-Kaelble approach, which makes it possible to estimate its components and predict the wettability of polymeric materials. At the same time, the issue of a comprehensive analysis of the relationship between the

surface energy of films and the wetting and adhesion of UV flexographic inks remains insufficiently studied.

The practical need for such studies is due to the constant expansion of the use of UV inks for flexographic printing in the production of packaging products, where increased requirements are imposed on print quality, ink layer stability, and image durability. The use of polypropylene and polyethylene terephthalate films without taking into account their surface energy can lead to insufficient wetting, ink layer peeling, reduced adhesion, and the emergence of defects during subsequent post-printing processes. Establishing the patterns of the influence of surface energy on the process of spreading UV flexographic inks could make it possible to optimize technological printing modes, justify the choice of materials, and increase print stability.

Taking the above into account, studies aimed at establishing the dependence of the wettability and adhesion of UV flexographic inks on the surface energy of polymer films are relevant.

2. Literature review and problem statement

The physical foundations of wettability, mechanisms of intermolecular interactions, as well as their role in the formation of the contact angle are considered in [7]. The authors analyzed in detail the interactions of permanent dipoles, induced dipoles, dispersion forces, and hydrogen bonds. The relationship between surface tension and the wetting angle is shown; the Young-Laplace equation describing the shape of a drop on a surface is considered. Special attention is paid to the method of a sessile drop and axisymmetric analysis of the drop shape to determine the wetting parameters. However, the work mainly considers the physical laws of wetting without analyzing their influence on the adhesion of printing inks to polymeric materials. The features of multicomponent ink systems, in which wetting does not always directly correlate with adhesion, are not considered.

A methodological basis for determining the surface energy of polymers is work [8], which proposes an approach to evaluating the surface free energy with its separation into polar and dispersion components. It is shown that the use of two test liquids makes it possible to determine the contribution of each component and to estimate the wettability of the surface. This method is widely used to study polymeric materials and predict the adhesive interaction. However, the work does not take into account the influence of surface morphology, roughness, as well as structural changes of the material during printing. In addition, the method was devised for idealized surfaces and does not take into account complex multicomponent ink systems, which limits its application for predicting adhesion in printing processes.

In [1], it is shown that the adhesion of inks to polymer films is determined by the ratio of the polar and dispersion components of the surface energy, which are estimated using the Owens-Wendt contact angles. It was found that polyolefins (PE, PP) due to their low polarity are characterized by poor wettability; therefore, they require preliminary modification of the surface or the composition of the inks.

In study [2], it was found that corona treatment significantly increases the adhesion of water-based inks to polymer films. This is due not only to the increase in surface energy but primarily to the formation of polar groups and a change in the surface microrelief. At the same time, the difference in

the values of surface energy between the ink and the polymer film has a secondary effect.

In work [5], the effect of the surface energy of polymer films on the wetting of UV flexographic inks was investigated. It was shown that an increase in the polar component of surface energy improves the wetting and adhesion of the ink. At the same time, it was found that even at high values of surface energy, wetting can be limited due to the predominance of cohesive forces in the ink. This indicates the need to match the properties of the ink and the substrate, and the effect of the rheological properties of the ink and the technological parameters of printing on the adhesive interaction was not considered.

The study on the effect of wettability on the interfacial adhesion of polymers is reported in [3]. The authors established a positive correlation between surface wetting and interfacial fracture energy. At the same time, it is shown that for multicomponent liquids, wettability analysis has limitations, since different components can migrate to the surface and change the nature of the interaction. The results indicate the complexity of using the contact angle as the only criterion for predicting adhesion. The studies were performed for the "elastomer-solid substrate" system and do not take into account the features of printing inks containing pigments, solvents, and additives.

In work [4], the relationship between surface energy, wetting, and water transfer in polymer films was investigated. It was shown that the introduction of sulfone groups into polymers leads to a decrease in the contact angle and an increase in surface hydrophilicity. The dependence of wettability on the chemical composition of ionomers and their structure was established. However, the effect of these changes on the adhesion of paints or coatings was not considered in the work since the studies concern membrane materials and mass transfer processes.

The influence of surface morphology on the wettability of polymeric materials was investigated in [9], in which polymeric surfaces were modified with copper nanoparticles. It was shown that with increasing nanoparticle height, wettability changes almost linearly, and the contribution to the change in the contact angle is made by the nanomeniscus formed between the nanoparticle and the substrate. The results demonstrate the important role of surface nanostructure in the formation of wettability but the issue of using nanostructuring to improve the adhesion of printing inks remains unresolved.

In [10], the possibilities of the Owens-Wendt method for analyzing the polarity of multicomponent systems and determining the contributions of surface energy are shown. The dependence of phase separation on the ratio of dispersion and polar forces was established. However, the study was conducted for model systems and the adhesive interaction of paints with polymeric materials was not considered as they are oriented on the physicochemical processes of phase separation.

Study [11] tackles the design of film composites based on water-soluble and biocompatible polyvinyl alcohol for the manufacture of flexible packaging and the study of their surface properties. By introducing glycerol and formic acid into the polymer composition, the hydrophilicity of the films increased. Such changes can be explained by the formation of polar molecular groups on the film surface. Due to their hydrophilic properties, they can be printed with water-based inkjet inks with high adhesive interaction.

The importance of surface properties of materials for the printing process was confirmed in [12], in which it was established that the surface properties of the material are one of the priority factors for the quality of flexographic printing. Predictive models of the influence of the parameters of the printing plate, ink and surface energy of the material were constructed. The work did not conduct experimental studies on the wettability of specific polymer materials and did not establish quantitative dependences of adhesion on surface energy.

In [6], the adhesive interaction of flexographic inks with photopolymer printing plates was studied. It was shown that the surface energy of the plates decreases during the printing process due to the diffusion of solvents and a change in the number of functional groups. The dependence of adhesion on the nature of the ink pigment was established. However, the issues of stabilizing surface properties and predicting adhesion during printing remained unresolved. The reason is the complexity of the processes of mutual diffusion and structural changes of the surface.

Methods for measuring the contact angle and the characterization of the surface of materials were considered in [13, 14]. It was shown that measuring the contact angle is a universal method for determining the wettability and hydrophilicity of surfaces. Recommendations for conducting measurements and analyzing data were given, but the issues of interpreting the results for predicting the adhesion of inks under actual printing conditions remained unresolved.

In addition to polymeric materials, the processes of wetting and interfacial interaction are also studied for inorganic surfaces. In [15], the surface energy of glass and the interfacial interaction at the “glass–metal” interface were analyzed. In [16], wetting and the evolution of the interfacial structure in systems based on oxide materials were considered, which allows us to assess the role of the chemical nature of the surface in the formation of adhesive contact. A separate group is made up of “metal-liquid” systems, for which in [17] the dependence of the surface tension on temperature and interatomic interaction was shown, which determines the wettability and the nature of the interfacial interaction. The results indicate that the energy characteristics of the surface determine the wettability and adhesive behavior regardless of the nature of the material, which is consistent with the approaches used to analyze polymer films.

Our review of literature sources shows that the issues of wettability and adhesion of inks to polymeric materials are widely studied; however, the relationship of these processes with surface energy under flexographic printing conditions remains insufficiently explored. At the same time, there is no comprehensive approach to assessing wetting and adhesion in the “flexographic ink – polymer film” system, taking into account actual printing conditions. The thermodynamic characteristics of interfacial interaction, which make it possible to quantitatively describe the wetting and adhesion processes, remain particularly insufficiently studied. This complicates the prediction of print quality and the justified choice of materials.

All this allows us to state that it is advisable to conduct a study aimed at establishing the regularities of wetting and adhesion of flexographic inks on polymer films with different surface energies.

3. The aim and objectives of the study

The aim of our study is to establish the regularities of wetting and adhesion of flexographic inks on

polymer films with different surface energies based on the determination of their thermodynamic characteristics. This will make it possible to reasonably select film materials for flexographic printing and predict the stability of adhesion of the ink layer.

To achieve this goal, the following tasks were set:

- to determine the equilibrium values of the cosine of the wetting angle of polymer films when interacting with liquids of different nature and flexographic ink;
- to calculate the work of adhesion for the “liquid – polymer film” systems;
- to determine the work of spreading and the work of recovery for the systems under study;
- to determine the components of the surface free energy of polymer films using the Owens-Wendt-Rabel-Kaelble method;
- to assess the wettability of flexographic ink on polymer films.

4. The study materials and methods

4.1. The object and hypothesis of the study

The object of our study is the process of wetting and adhesive interaction of flexographic inks with polymer films of different nature and surface structure.

The principal hypothesis assumes the determining influence of the ratio of the polar and dispersion components of surface energy on wettability and adhesive interaction in the “liquid – polymer film” system.

The study assumes the isothermal nature of the wetting process and the absence of a chemical reaction between the liquid and the film surface.

As a simplification, the film surface is considered energetically homogeneous, and the drop shape is considered as a segment of a spherical surface.

4.2. Materials under investigation used in the experiment

Four types of polymer films used in the production of packaging products and labels for flexographic printing were used for experimental research. The samples under investigation included three polypropylene (PP) films of different thicknesses and surface types (glossy, matte) and one polyethylene terephthalate (PET) film. The choice of materials is due to their wide industrial use and the need to evaluate their wettability and adhesion to printing inks.

The characteristics of the films under investigation are given in Table 1.

Table 1

Characteristics of the studied polymer films

Sample No.	1	2	3	4
Material	Polypropylene (PP)	Polypropylene (PP)	Polypropylene (PP)	Polyethylene terephthalate (PET)
Surface type	Glossy	Matt	Glossy	Glossy
Weight, g/m ²	32.25	18.05	18.75	17.55
Thickness, μm	36	22	22	21
Density	0.896	0.820	0.852	0.836
Main application	Packaging films, labels	Packaging with a decorative surface	Thin flexible packaging	High-quality packaging, labels

Polypropylene films have a predominantly nonpolar macromolecular structure, which causes low surface energy and dominance of the dispersion component of interfacial interaction.

Polyethylene terephthalate film contains ether and aromatic groups in its structure, which increases the polarity of the surface and promotes specific intermolecular interactions.

Liquids with different polarity and surface tension were used to study wetting. This approach is used to determine the dispersion and polar components of the surface energy of solids by the Owens-Wendt-Rabel-Kaelble (OWRK) method [18].

The list and physicochemical characteristics of the liquids are given in Table 2.

Table 2
Physical-chemical characteristics of the studied liquids ($T = 20^\circ\text{C}$)

Liquid	Surface tension γ_L , mN/m	Dispersion component γ_L^d , mN/m	Polar component γ_L^p , mN/m
Decane	23.8	23.8	0
1,4-dioxane	36.0	36.0	0
Dimethylformamide (DMF)	37.1	32.0	5.1
Dimethyl sulfoxide (DMSO)	43.5	36.0	7.5
Ethylene glycol (EG)	47.7	29.0	18.7
Distilled water (DW)	72.8	21.8	51.0

Nonpolar liquids (decane, 1,4-dioxane) were used to determine the dispersion component of the surface energy of the films. Polar liquids (distilled water (DW), ethylene glycol (EG), dimethylformamide (DMF), dimethyl sulfoxide (DMSO)) were used to evaluate the contribution of specific intermolecular interactions.

The value of the surface tension of liquids (γ_L) was taken from the CRC Handbook of Chemistry and Physics (USA) [19], and the dispersion (γ_L^d) and polar (γ_L^p) components were taken from the literature data used in the Owens-Wendt method [15].

4.3. Determining the contact angles of wetting

We determined the geometric parameters of the drop and the processing of the results by using an optical-digital image analysis system that corresponds to current approaches to measuring contact angles and determining surface energy by the Owens-Wendt method [10]. This method is widely used to assess the wettability of solid surfaces by various liquids.

The studies were carried out using a tele optical-digital drop image registration system. The system consisted of a Logitech Quick Cam digital camera (USA) with a CCD matrix of 640×480 pixels and a Jupiter-37A lens (Ukraine) with a focal length of 135 mm.

A 10×10 mm polymer film sample was fixed on a horizontal stage of the installation. A drop of the liquid under study was applied to the sample surface using a dispenser.

The image of the drop was recorded with a digital camera. Visualization of drops is used for qualitative assessment of the drop shape and the nature of surface wetting. The obtained image was transferred to a personal computer for further processing.

From the digital image, the geometric parameters of the drop were determined: the diameter of the contact zone of the drop with the sample surface d and the height of the drop segment h .

The cosine of the contact angle was determined from the following relation

$$\cos \theta = \frac{\left(\frac{d}{2}\right)^2 - h^2}{\left(\frac{d}{2}\right)^2 + h^2}, \quad (1)$$

where d is the diameter of the droplet contact zone with the sample surface;

h is the height of the droplet segment;

θ is the contact angle.

The geometric parameters of the droplet and the cosine of the contact angle were determined using the software "Analysis of Liquid Spreading Kinetics" (Ukraine) [20].

This program was also used to determine the main thermodynamic characteristics of wetting: work of adhesion, work of cohesion, work of spreading, and work of recovery for the "liquid - polymer film" system.

For each "liquid - polymer film" system, the change in the contact angle over time was recorded. The value of the contact angle 180° after the droplet application was considered to be equilibrium.

The study was carried out at a temperature of $20 \pm 1^\circ\text{C}$.

4.4. Determining the thermodynamic characteristics of wetting

To evaluate the interaction of liquids with the surface of polymer films, the main thermodynamic characteristics of wetting were determined. These include work of adhesion, work of cohesion, work of spreading, as well as work of recovery.

Work of cohesion, work of spreading, and work of recovery were considered as auxiliary thermodynamic characteristics that allow for a more complete characterization of the wetting process and interpretation of the value of the work of adhesion.

The work of adhesion between a liquid and a solid surface is determined based on a thermodynamic approach. According to the Dupre equation [21], the work of adhesion can be represented as the sum of the surface energies of the phases

$$W_a = \gamma_s + \gamma_L - \gamma_{SL}, \quad (2)$$

where γ_s is the surface energy of the solid, γ_L is the surface tension of the liquid, and γ_{SL} is the interfacial energy at the solid-liquid interface.

In practical studies, this equation is combined with the Young equation, which leads to the Young-Dupre equation

$$W_a = \gamma_s (1 + \cos \theta), \quad (3)$$

where W_a is the work of adhesion, mN/m;

γ_L is the surface tension of the liquid, mN/m;

θ is the contact angle.

The work of cohesion of the liquid was determined from the following relation

$$W_k = 2\gamma_L, \quad (4)$$

where W_k is the work of cohesion, mN/m;

γ_L is the surface tension of the liquid.

The work of spreading a liquid on the surface of a solid was determined from the following formula

$$W_r = W_a - W_k, \tag{5}$$

where W_r is the work of spreading, mN/m.

For additional assessment of the energy characteristics of wetting, the work of recovery was determined

$$W_{\text{àññ.}} = \frac{W_a}{W_k}. \tag{6}$$

The calculation of the thermodynamic characteristics of wetting was performed using the software “Analysis of Liquid Flow Kinetics” (Ukraine) [21]. The program automatically processes the geometric parameters of the droplet and determines the corresponding energy characteristics of the “liquid – polymer film” system. The obtained values were used for further processing and interpretation of the wettability data in the “liquid-polymer film” system.

4. 5. Determining the surface energy components by the Owens-Wendt-Rabel-Kaelble (OWRK) method

The surface energy components of polymer films were determined by the OWRK method [22]. The method is based on the separation of surface energy into dispersion and polar components.

The equilibrium contact angle of wetting and the physicochemical characteristics of the studied liquids were used for the calculation.

According to the OWRK method, the interaction between a liquid and a solid surface is described by the following equation

$$\gamma L(1 + \cos\theta) = 2\sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^p \gamma_L^p}, \tag{7}$$

where γL is the surface tension of the liquid, mN/m;

$\cos\theta$ is the contact angle;

γ_s^d, γ_s^p are the dispersion and polar components of the surface energy of the solid, mN/m;

γ_L^d, γ_L^p are the dispersion and polar components of the surface tension of the liquid, mN/m.

The surface energy of the solid was defined as the sum of its components

$$\gamma_s = \gamma_s^d + \gamma_s^p. \tag{8}$$

For the calculation, a set of polar and non-polar liquids with known values γ_L^d, γ_L^p was used. This allowed us to obtain a system of equations and determine the components of the surface energy of the studied films.

The processing of experimental data and determining the γ_s, γ_s^d and γ_s^p values were carried out on the basis of the values of the contact angles of wetting.

The results were used for further processing of the experimental data.

4. 6. Statistical processing of results

Each experimental measurement was performed at least five times.

The average values of the obtained values were used to process the results.

The error was defined as the deviation of the results of individual measurements from the average value.

The processing of experimental data was performed using standard tools of the Microsoft Excel spreadsheet (USA).

5. Results of investigating the wetting and surface energy of polymer films

5. 1. Analysis of contact angles of wetting

The wettability of polymer films was evaluated by the values of the cosine of the contact angle of wetting. Table 3 gives values of the cosine of the contact angle of wetting ($\cos\theta$) for the studied polymer films when interacting with liquids of different nature, as well as UV flexographic ink (UVFI).

Table 3

Cosine of the equilibrium wetting angle ($\cos\theta$) of polymer films at $t = 180$ s

Sample No.	Decane	DMF	1,4- Dioxane	DMSO	EG	DW	UVFI
1	0.93	0.95	0.99	0.94	0.64	0.64	0.86
2	0.91	0.96	0.99	0.94	0.36	0.36	0.7
3	0.96	0.83	0.91	0.94	0.91	0.92	0.85
4	0.93	0.98	0.98	0.82	0.91	0.86	0.94

The $\cos\theta$ values vary depending on the polarity of the liquid. For non-polar liquids such as decane and 1,4-dioxane, the $\cos\theta$ values for all samples are high and range from 0.9 to 0.99, which corresponds to high surface wettability values of the polymers.

For polar liquids, the $\cos\theta$ values vary. The lowest $\cos\theta$ values are observed for water and ethylene glycol, especially for sample 2. For this sample, the $\cos\theta$ is 0.36, which corresponds to lower wettability values. For samples 3 and 4, higher $\cos\theta$ values are observed when interacting with polar liquids. The $\cos\theta$ value is 0.92, which corresponds to higher surface wettability values.

For UV flexographic ink, the $\cos\theta$ values are in the range from 0.7 to 0.94, which corresponds to medium wettability values. The highest $\cos\theta$ values are observed for samples 3 and 4.

5. 2. Analyzing the work of adhesion

Fig. 1 shows the values of work of adhesion (W_a) for the “liquid-polymer film” systems at equilibrium.

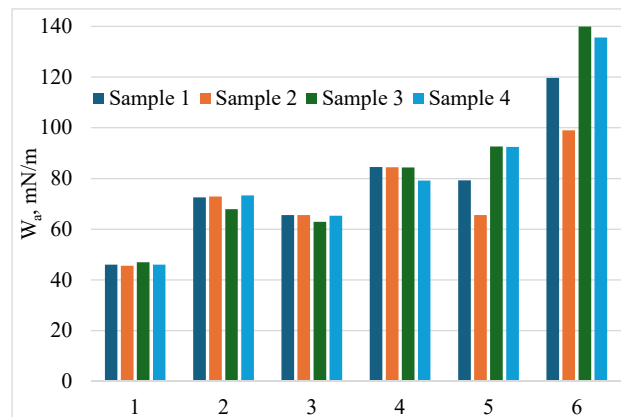


Fig. 1. Values of the work of adhesion (W_a) for systems “liquid – polymer film”: 1 – decane; 2 – dimethylformamide (DMF); 3 – 1,4-dioxane; 4 – dimethyl sulfoxide (DMSO); 5 – ethylene glycol (EG); 6 – distilled water (the numbering corresponds to the designations on the abscissa axis)

Values for the work of adhesion vary depending on the nature of the liquid. The lowest W_a values are observed for decane and are in the range of 45–47 mN/m for all the samples studied.

For organic solvents of medium polarity (dimethylformamide, 1,4-dioxane, dimethyl sulfoxide), the W_a values are 60–85 mN/m; with higher W_a values observed for dimethyl sulfoxide.

The highest values of the work of adhesion were obtained for ethylene glycol and water. For water, W_a is 120–140 mN/m.

For samples 3 and 4, higher values of the work of adhesion are observed for polar liquids.

Sample 2 demonstrates the lowest values of the work of adhesion for polar liquids, in particular for water and ethylene glycol.

5. 3. Analyzing the work of spreading and recovery

Table 4 gives values for the work of spreading (W_s) and the work of recovery (W_{rec}) at equilibrium wetting ($t = 180$ s).

Table 4

Work of spreading (W_s) and work of recovery (W_{rec}) at equilibrium wetting ($t = 180$ s)

Sample No.	Decane	DMF	1,4- Dioxane	DMSO	EG	DW	UVFI
W_{rec}							
1	0.96	0.98	0.99	0.97	0.82	0.82	0.93
2	0.95	0.98	0.99	0.97	0.68	0.68	0.85
3	0.98	0.91	0.95	0.97	0.96	0.96	0.93
4	0.96	0.99	0.99	0.91	0.96	0.93	0.97
W_s , mN/m							
1	-1.75	-1.68	-0.39	-2.51	-17.54	-25.92	-5.44
2	-2.21	-1.34	-0.53	-2.59	-31.20	-46.60	-11.94
3	-0.86	-6.33	-3.09	-2.66	-4.14	-5.66	-5.93
4	-1.73	-0.83	-0.65	-7.81	4.31	-9.93	-2.47

Table 4 gives negative W_s values for most of the studied systems. In particular, for water, the W_s value ranges from -25.92 to -46.60 mN/m.

The lowest W_s values are observed for sample 2. Higher W_s values are observed for samples 3 and 4. In particular, for sample 4, when interacting with ethylene glycol, a positive W_s value (4.31 mN/m) is observed.

The values of the work of recovery (W_{rec}) for most of the studied liquids are 0.82–0.99. For polar liquids (water, ethylene glycol), a decrease in the W_{rec} values for sample 2 (to 0.68) is observed.

Fig. 2, 3 show the shape of the drops of the studied liquids when the equilibrium state of wetting is reached ($t = 180$ s).

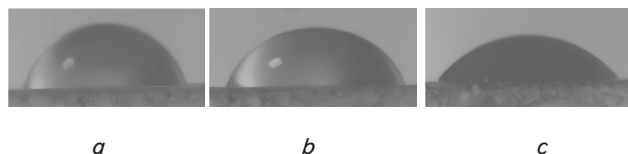


Fig. 2. Visualization of the shape of liquids during equilibrium wetting ($t = 180$ s) on the surface of a polymer film (sample 2): *a* – distilled water; *b* – ethylene glycol; *c* – UV flexographic ink

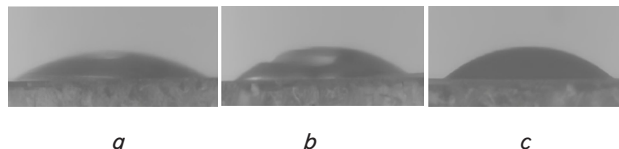


Fig. 3. Visualization of the shape of liquid droplets during equilibrium wetting ($t = 180$ s) on the surface of a polymer film (sample 3): *a* – distilled water; *b* – ethylene glycol; *c* – UV flexographic ink

In Fig. 2, 3, differences in the shape of the drops are observed for different samples. For sample 2, drops of water, ethylene glycol, and UV flexographic ink have a more pronounced spherical shape. For sample 3, spreading of the drops and a decrease in their height are observed.

5. 4. Determining the surface energy of polymer films

Table 5 gives values for the surface energy of polymer films and its components, determined by the Owens-Wendt method [10].

Table 5

Surface free energy parameters of polymer films determined by the Owens-Wendt method

Sample No.	γ_s , mN/m	γ_s^d , mN/m	γ_s^p , mN/m	γ_s^p / γ_s
1	46.8	42.1	4.7	0.10
2	42.3	39.5	2.8	0.07
3	52.6	43.8	8.8	0.17
4	50.9	41.2	9.7	0.19

The surface energy values of the studied films are 42–53 mN/m. The lowest surface energy value is characteristic of sample 2 (42.3 mN/m). The highest surface energy values are observed for samples 3 and 4. For all samples, the dispersion component of the surface energy prevails. At the same time, an increase in the polar component is observed for samples 3 and 4. The value of the polar fraction (γ_s^p / γ_s) for sample 2 is the lowest, while for samples 3 and 4 it is higher.

5. 5. Assessing the wettability of UV flexographic ink

Table 6 gives values for the equilibrium cosine of the wetting angle and the work of adhesion of the ink for the studied samples.

Table 6

Values of the work of adhesion and the equilibrium wetting angle of the UV flexographic ink on the surfaces of the samples

Sample No.	1	2	3	4
$\cos\theta$	0.86	0.7	0.85	0.94
W_a	74.56	68.06	74.07	77.53

The lowest value of the work of adhesion corresponds to sample 2 (68.06 mN/m). Samples 3 and 4 are characterized by higher W_a values (74.07–77.53 mN/m). The W_a value for sample 1 is 74.56 mN/m. The lowest value of $\cos\theta$ is characteristic of sample 2 (0.7), while the highest is characteristic of sample 4 (0.94).

Fig. 4 shows a comparison of values for the work of adhesion of UV flexographic ink and ethylene glycol.

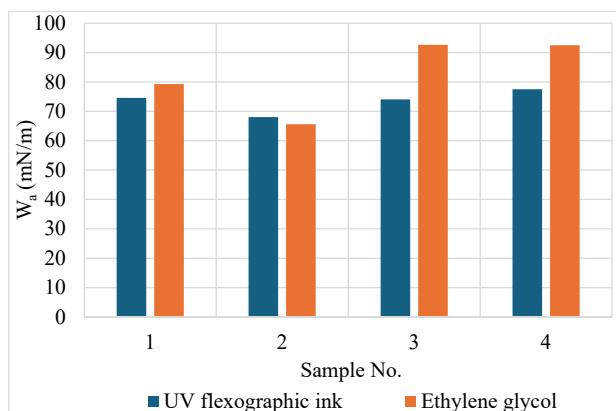


Fig. 4. Comparing the adhesion performance of UV flexographic ink and ethylene glycol

The work of adhesion values of the ink are close to those for ethylene glycol. Samples 3 and 4 are characterized by increased W_a values for both liquids, while sample 2 has the lowest W_a values.

6. Discussion of results based on the wetting and adhesion interaction in the systems “liquid-polymer film”

Our results make it possible to generalize the regularities of wetting of polymer films of different nature and to establish a connection between their surface energy and adhesive interaction with liquids. This is confirmed by the data in Tables 3, 5 in which the dependence of the values of $\cos\theta$ and the work of adhesion on the ratio of the dispersion and polar components of the surface energy is established.

It is established that the wettability of the studied materials is determined by the ratio of the dispersion and polar components of the surface energy. For non-polar liquids, all samples are characterized by high values of $\cos\theta$ and stable values of the work of adhesion, which indicates the dominance of dispersion interactions.

For polar liquids, a clear differentiation of wettability is observed depending on the nature of the polymer. Samples 3 and 4 demonstrate increased work of adhesion values and better wettability, which is consistent with the increase in the polar component of their surface energy. This confirms the decisive role of polar interactions in the formation of adhesive contact. This is explained by the presence of specific intermolecular interactions (dipole-dipole and hydrogen), which enhance the adhesion between the liquid and the polymer surface.

Sample 2 is characterized by the lowest values of $\cos\theta$ and work of adhesion for polar liquids, which indicates a limited ability to interfacial interaction. This behavior is associated with the features of the surface structure and its energy characteristics.

It is important to note that the studied samples 1–3 are made of the same material (polypropylene) but differ in the type of surface and physical characteristics (thickness, mass). This allows us to assess the influence of not only the chemical nature of the polymer but also the structural features of the surface on the wetting process.

Unlike studies [23, 24], in which most attention was paid to the influence of operational factors on the mechan-

ical properties of polymer films, in this work a quantitative relationship between surface energy and wettability was established. This became possible due to determining the polar and dispersion components of surface energy and the analysis of their ratio. This approach allows us to assess the adhesive interaction and predict the wettability of polymer materials. The results, in particular the established dependences of the values of $\cos\theta$ and the work of adhesion on the ratio of the polar and dispersion components of surface energy, are consistent with modern ideas about the determining role of surface energy in the formation of interfacial interaction [1, 18]; however, unlike existing approaches [10], they provide a quantitative assessment of the contribution of its components to the wetting process.

It was found that even with the same chemical nature of the material, wettability can differ significantly. The matte surface (sample 2) is characterized by worse wettability compared to glossy samples, which is due to a more developed microrelief and a decrease in the effective area of contact of the liquid with the surface, which, in turn, leads to a decrease in the adhesive interaction.

The influence of the thickness and mass of the films is manifested in a change in their surface characteristics, which is reflected in the variation of the values of the work of adhesion and the wetting angle.

For most of the studied systems, limited wetting is realized, which corresponds to negative values of the work of spreading. For some cases, an improvement in spreading is noted, which is important for the formation of a continuous ink layer.

The adhesive behavior of UV flexographic ink is comparable to polar liquids, which is confirmed by the close values of the work of adhesion for the ink and ethylene glycol. This indicates the presence of polar interaction mechanisms in the “ink-polymer film” system and explains the effectiveness of wetting polymer surfaces with ink.

The established values for the work of adhesion and the wetting angle are consistent with the determined values of surface energy and demonstrate the possibility of predicting the wettability of polymeric materials based on their energy characteristics, which is important for the selection of “ink-substrate” systems in flexographic printing.

Our study has certain methodological limitations. In particular, the assessment of the adhesive interaction was carried out mainly on the basis of thermodynamic characteristics without direct experimental determining the strength of the adhesive bond. In addition, the work did not take into account the rheological properties of the inks, which can significantly affect the wetting process and coating formation. The influence of technological printing parameters, in particular the speed of ink application and drying conditions, which can change the nature of the interfacial interaction, was not investigated either.

These shortcomings might be eliminated in further studies by combining thermodynamic analysis with experimental determining the adhesive strength, as well as taking into account the rheological and technological parameters of the printing process.

The study was performed for the original surfaces of polymer films without additional modification, which determines the limits of application of our results. Under industrial conditions, wettability may change due to surface activation, in particular corona treatment, which requires additional consideration in practical use.

7. Conclusions

1. The equilibrium values for the cosine of the wetting angle of polymer films when interacting with liquids of different nature have been determined. It was established that for nonpolar liquids the values of $\cos\theta$ are high (0.90–0.99), while for polar liquids they decrease to 0.36–0.92, which is due to differences in intermolecular interactions.

2. The work of adhesion for the “liquid-polymer film” systems was calculated and its dependence on the polarity of the liquid was established. It was shown that for nonpolar liquids, the W_a values are 45–47 mN/m, while for polar liquids they increase to 120–140 mN/m due to the contribution of polar interactions.

3. The work of spreading was determined, and it was established that for most of the studied systems limited wetting is realized, which corresponds to negative W_s values. At the same time, for some systems (ethylene glycol, sample 4) a positive W_s value is observed, which indicates the possibility of spontaneous spreading.

4. The components of the surface free energy of polymer films were determined by the Owens-Wendt-Rabel-Kaelble method, and it was found that for all samples the dispersion component prevails, and an increase in the polar component leads to an improvement in wettability and an increase in the work of adhesion.

5. The wettability of flexographic ink on polymer films was evaluated, and it was found that its adhesive behavior is similar to polar liquids, which is confirmed by the close values of the work of adhesion and indicates the presence of polar mechanisms of interaction in the “ink-polymer film” system.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal,

authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

During the preparation of the manuscript, artificial intelligence tools ChatGPT (OpenAI, GPT-5.3) were used to linguistically edit the text, clarify scientific formulations, and improve the structure of the presentation of the material. AI tools were used in the preparation of the introduction, literature review, and formulation of conclusions.

The results were verified by the authors by comparing them with experimental data, analytical calculations, and published scientific sources. All numerical values, dependences, and interpretations were formed by the authors independently.

Artificial intelligence tools were not used to obtain, process, or interpret experimental results.

The use of AI did not affect the scientific results and conclusions of the study.

Authors' contributions

Valentyna Slobodianyuk: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing – original draft, Visualization; **Ivanna Koniukhova:** Methodology, Supervision, Writing – review & editing.

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